

# **NEW NITROSYLATING AGENTS** **[ THIONITRITES & ALKYL NITRITES ]**

*A Thesis Submitted*  
In Partial Fulfilment of the Requirements  
for the Degree of

**DOCTOR OF PHILOSOPHY**

*by*

**DAYA SHANKAR PANDEY**

*to the*

**DEPARTMENT OF CHEMISTRY**

**INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

**AUGUST, 1988**

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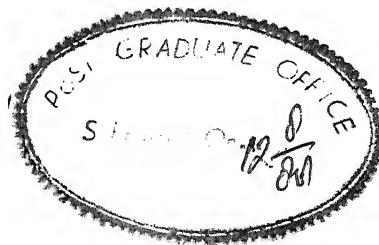
STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Prof. U.C. Agarwala.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.



DAYA SHANKAR PANDEY



CERTIFICATE

Certified that the work contained in this thesis, entitled:  
NEW NITROSYLATING AGENTS [THIONITRITES AND ALKYL NITRITES] has been  
carried out by Mr. Daya Shankar Pandey, under my supervision and  
the same has not been submitted elsewhere for a degree.

A handwritten signature in cursive script, appearing to read "U.C. Agarwala".

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Professor of Chemistry,  
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Kanpur  
August 1988

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CERTIFICATE OF COURSE WORK

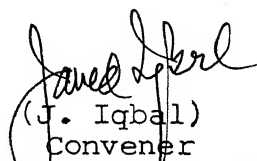
This is to certify that Mr. Daya Shankar Pandey has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

Chm 505	Principles of Organic Chemistry
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Chm 545	Principles of Inorganic Chemistry
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Chm 800	General Seminar
Chm 801	Special Seminar
Chm 900	Ph.D. Thesis

Mr. Daya Shankar Pandey was admitted to the candidacy of the Ph.D. degree programme in October 1984, after he successfully completed the written and oral qualifying examinations.



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Daya Shankar Pandey

## PREFACE

The thesis has its roots in the study of transition metal nitrosyl complexes which have versatile applications as catalysts, as precursors for many novel complexes and in overcoming a number of problems related to pollution control. Despite an enormous amount of synthetic and structural work in the area of nitrosyls, development of new simpler synthetic procedures is still of immense interest. Indeed even today, nitric oxide has been preferentially used for metal nitrosylation, in general, besides the use of alternative nitrosylating agents like,  $\text{RNO}_2$ , hydroxylamines, NOX and N-nitrosamides. The latter could not possibly be utilized in a generalized way. Another point of general importance connected with the synthetic agents is that a few of them (NO, NOX) are hazardous gases while some are carcinogenic (nitrosamines) in nature. The hazardous nature of NO itself is well established. Such problems led to the synthetic chemists of today face a challenge of developing nitrosylating agents having general applicability similar to that of NO but having non hazardous nature. Though to achieve the aim is a difficult task, the work in the thesis exhibits an attempt in the direction. Since S-nitroso organic compounds (penicillamine thionitrite, trityl thionitrite, S-nitrosocysteine, and nitrosothiourea) contain easily cleavable (both chemically and photochemically) S-N bond, to take the advantage of its weakness to generate NO in situ for its trapping by the metal ions/or their complexes could be a good starting point

for examining their synthetic potentialities. Another point in favour connected to thionitrites besides the medicinal values is their nonhazardous nature. In addition, it is also felt that a large variation in their thermal half lives could provide a specificity of a particular thionitrite for the synthesis of a particular set of metal nitrosyls.

The scope, the object of the work and a brief literature survey regarding the synthetic procedures, modes of bonding, reactivity of transition metal nitrosyls, various theories, rules and techniques for understanding the bonding and distinguishing linear nitrosyl groups from bent ones are described in the first chapter.

Synthetic procedures of a number of metal nitrosyl complexes using penicillaminethionitrite at elevated temperatures have been described in chapter two.

Chapter three deals with the reactions of triethylthionitrite with metal salts and their complexes of Ru, Rh, Ir, Cr, Fe, Co, Ni, Mo and W in presence of coligands ( $\text{PPh}_3$ ,  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ , ethylenediamine, pyridine, bipyridyl, diethyldithiocarbamate, ammonium thiocyanate and acetylacetone) at elevated as well as at low temperatures.

Chapter four deals with reactions of S-nitrosocysteine with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ,  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ , in presence of triphenylphosphine,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in presence of 2,2-bipyridyl and lithium perchlorate,  $[\text{RuCl}_2(\text{PPh}_3)_3]$  and  $[\text{RhCl}(\text{PPh}_3)_3]$ . These reactions resulted in the

formation of a few new nitrosyl complexes. Their physical and chemical properties have been studied. Their possible structures have been proposed on the basis of the results of various physico-chemical techniques.

Fifth chapter describes the reactions of nitrosothiourea with Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II) and Hg(II) salts in the presence of coligands (pyridine, 2,2'-bipyridyl, 1,10-phenanthroline) and with a few complexes of ruthenium, rhodium, iridium, palladium and platinum at various temperatures. New nitrosyls and thiocyanato complexes, thus obtained, have been characterized using various physicochemical techniques. Their possible structures have also been proposed.

Synthesis of nitrosyl complexes of Cr, Fe and Co is presence of different coligands (maleonitrile dithiolate, 2,2'-bipyridyl, 1,10-phenanthroline, 7-aminoquinoline, acetylacetonethylenediamine, and salicylaldehyde ethylenediamine) at room and low temperatures using alkyl nitrites (methyl, ethyl, propyl and n-butyl) as nitrosylating agents have been described in chapter six.

A comparison of various S-nitrosoderivatives used for nitrosylation reactions has been briefly discussed in chapter seven.

Chapter eight summarizes all the work described in the thesis along with a few proposals for the future work.

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## CHAPTER ONE

### INTRODUCTION

During the past couple of decades a great interest arose in the study of metal nitrosyls because of their unique reactivity and their use as catalysts in many reactions. Ruthenium nitrosyls have been used in introducing N-C bond in many organic compounds and conversion of poisonous CO gas into CO<sub>2</sub> [1-9], rhodium and iridium ones, as catalysts [10-17] and in the synthesis of novel rhodium and iridium complexes [18-45]. Despite a large number of metal nitrosyl syntheses procedures available in the literature, the one related to the interaction of gaseous NO with metal ions and their complexes is still preferred over others. However its thermodynamic instability coupled with its being a menacing pollutant sometimes puts a constraint on its being of generalized applicability. One is, therefore, bound to rethink towards designing new synthetic procedures. One possible route could be in situ generation of NO by the cleavage of weak S-NO bond or O-NO bond with its subsequent trapping by metal ions. One possible advantage

of such a procedure will be that because of generating it inside the system itself, there is a low possibility of pollution due to NO.

The study connected to transition metal nitrosyl synthesis, reveals that the trans nitrosation reactions using a range of transfer nitrosating agents like alkyl nitrites, nitrosamines, NOX ( $X = Cl^-$ ,  $Br^-$ ,  $Br_3^-$  and  $NO_2^-$ ) have also been widely used for the nitrosyl synthesis. One of the reasons for this upsurge of interest resulted, at least in part, from the attempts for finding new nitrosylating agents. In all these systems, advantage has been taken from the weakness of O-N or N-N bonds. Literature survey however indicates practically no work towards in situ trapping of NO by the metal ions, generated by the cleavage of weak S-N bond despite their large applications to effect the nitrosation of alcohol and secondary amines [46]. Thionitrites lends particularly well to such a study because of very large variations in their half lives (from a few seconds to months) of their thermal decomposition. They, undergo homolytic S-N bond cleavage both thermally and photochemically [47]. Since such a process has successfully been utilized in the synthesis of C-nitroso compounds and in the nitrosation reactions of amines and alcohols [48], it has a potentiality of being a good nitrosylation process too, according to which NO generated in situ by thermal decomposition of S-N bond of S-nitroso derivatives will be trapped by the metal ions and their complexes. Temperature dependence of S-N bond cleavage in S-nitrosoderivatives

will further add to the interest, because in most of the cases, the percentage yield of the nitrosyl products, using NO as a nitrosylating agent, is temperature dependent (some nitrosyls can not be synthesized even at room temperature) [49]. Thus by choosing a particular set of S-nitrosoderivatives one may be able to synthesize only a particular set of metal nitrosyls. For example, a set of thionitrites like those decomposing at elevated temperatures, may be specific for the synthesis of those which are formed at higher temperatures and vice versa.

Another series of compounds of equal promise are alkyl nitrites. Because of the weakness of the O-NO bond, thermal cleaving of the latter with subsequent trapping of NO by the metal ions, may provide another synthetic route of metal nitrosyls with NO generation in the system itself. It should be appreciated here that the ease of alkyl nitrite formation parallels that of their hydrolysis under acidic conditions yielding  $\text{HNO}_2$  [50]. Literature cites practically no work in this direction except the use of pentyl and isopentyl nitrites used as nitrosylating agents and that too, only in a couple of reactions [51-56] and methyl, ethyl, propyl and n-butyl nitrite [57] for the synthesis of metal nitrosyls at higher temperatures. A detailed study of reactions of various alkyl nitrites under varying reaction conditions therefore warrants further attention for their utility in the metal nitrosyl synthesis.

The present work concerns with the experimental details of the use of thionitrites and alkyl nitrites in the metal nitrosyl synthesis and with the discussion of the results obtained therefrom.

Reactions of various metal ions and their complexes with four S-nitrosoderivatives (penicillaminothionitrite, trityl thionitrite, S-nitrosocysteine and nitrosothiourea) having different thermal stabilities towards denitrosation have been carried out under varying reaction conditions. HCl, chlorine gas or/and  $\text{HgCl}_2$  have been used as catalyst and as a source of chloride ions, wherever necessary.

Reaction of penicillamine thionitrite with different metal ions and with the complexes of ruthenium, rhodium, iridium, cobalt and molybdenum yielded pure nitrosyl complexes in reasonably good yields (ca 70%) in presence or in the absence of  $\text{HgCl}_2$  or HCl gas at elevated temperatures. The results suggested smooth denitrosation of penicillamine thionitrite at elevated temperatures in alcoholic medium affording metal nitrosyls with yields comparable to those when MNTS was used for nitrosylation. A great promise has thus, been shown by penicillamine thionitrite as a versatile nitrosylating agent.

Reactions of trityl thionitrite with ruthenium metal and its complexes could not yield the pure nitrosyl complex in absence of  $\text{HgCl}_2$  or HCl gas. Rather it gave sulfide containing complex.

In presence of  $\text{HgCl}_2$  or  $\text{HCl}$  gas, the literature known nitrosyl  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$  was obtained. Its reactions with rhodium and iridium salts in presence of coligands and their complexes yielded pure nitrosyls indicating the importance of the use of  $\text{HgCl}_2$  or  $\text{HCl}$  gas in the denitrosation process.

Reactions of S-nitrosocysteine with ruthenium and rhodium salts and their complexes did not yield the literature known pure nitrosyls in the absence of catalysts in the presence of  $\text{HgCl}_2$  pure nitrosyl complexes were obtained. In its absence it yielded nitrosyl products containing disulfide formed as a result of denitrosation.

Reactions of nitrosothiourea with different metal ions of the first transition series yielded thiocyanato complexes, in the reaction conditions under which the nitrosyls have previously been synthesized. Only those metals which have very high affinity for nitrosyl group, on reacting with nitrosothiourea yielded the nitrosyl complexes, suggesting that it may not be used as a good nitrosylating agent.

Although the nitrosylation reactions using alkyl nitrites as nitrosylating agent at higher temperatures have been carried out by Khan et al [57]. In order to examine their general applicability for nitrosylation, reactions of alkyl nitrites ( $\text{RONO}$ ,  $\text{R} = \text{Methyl, Ethyl, Propyl and n-Butyl}$ ) with different metal ions and complexes of the first transition metal series have been carried out under varying reaction conditions at room and lower temperatures.

## I.2 Chemistry of Transition Metal Nitrosyls

A number of review articles dealing with nitrosyl chemistry at length are available in the literature [58-74]. Though a few of those are comprehensive [59,63,65] the majority are concerned with the particular aspects, like their structures and bonding [64, 66,72], synthetic routes [68], organometallic nitrosyls [61], reactions of coordinated nitrosyl group [70,72], transition metal nitrosyls in pollution control and organic synthesis [73], etc. Since the decade beginning 1974 has seen an enormous increase in the studies of metal nitrosyls, the following overview is an effort to update the most recent accessible review on metal nitrosyls. Further emphasis will be given on their synthetic methods, reactivity, bonding and structural aspects. No attempt will be made to cover the chemistry of all the elements. It is limited to the latest significant developments in the nitrosyl chemistry of Ru, Co, Rh, Ir, Mo and W.

### I.2A Synthetic Routes

The different main pathways to synthesize the metal nitrosyls are, (1) Direct insertion of NO, (2) reactions of ionic nitrosonium salts, (3) reactions of NOX ( $X = Cl^-$ ,  $Br^-$ ,  $Br_3^-$ ,  $NO_2^-$ ), (4) reaction of alkyl and alkali metal nitrites, (5) reactions of nitrosamides, (6) reactions of hydroxylamines, (7) reactions of nitric acid, (8) reactions of bis(triphenylphosphine)nitrogen (+1) nitrite and (9) reactions of transition metal nitrosyls. Of these routes, the

first has been very widely used while the potential of (4), (5), (8) and (9) are now in the process of being studied.

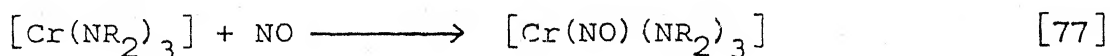
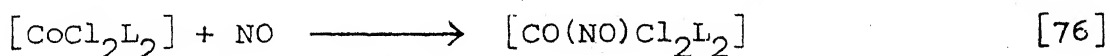
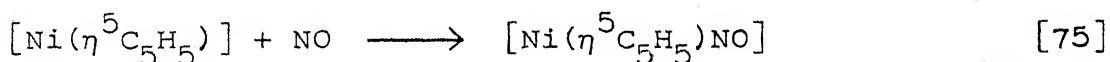
### A.1 Nitric Oxide

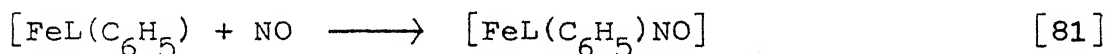
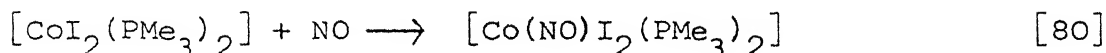
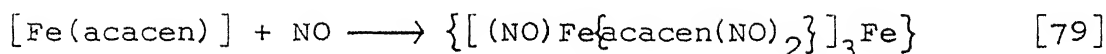
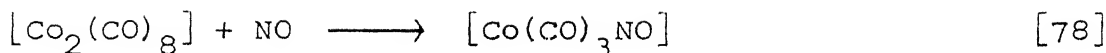
Easy availability, high product-yield with concomitantly fewer side reaction products, less unusual reaction conditions are a few attributions that favour the applicability of nitric oxide in the transition metal nitrosyl synthesis. Unlike carbonyl compounds, where high temperature and high pressure reactions are employed for the synthesis, nitric oxide has not been used under these conditions because of its oxidising properties and thermodynamic instability, some of the synthetic applications are as follows:

#### A.1(a) Addition of Nitric Oxide

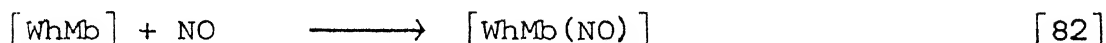
Introduction of NO group takes place in complexes containing 17 or 15 electron configuration so that NO can supply either one (NO acting as  $\text{NO}^-$ ) or three (NO acting as  $\text{NO}^+$ ) electrons to achieve the inert gas configuration.

Thus,



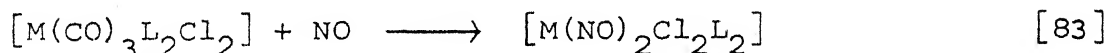


(L = octaethylporphyrin)

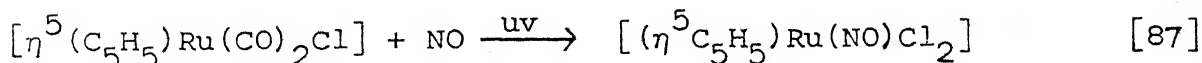
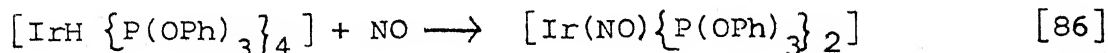
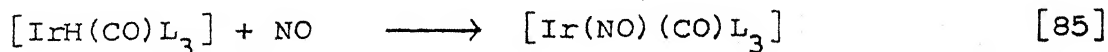
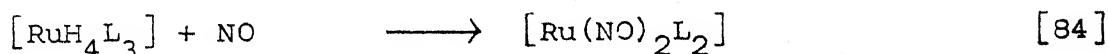
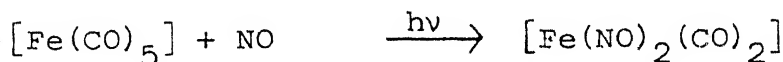


#### A.1(b) Substitution of ligands by nitric oxide

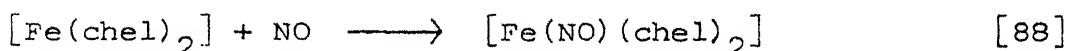
In the substitution reactions of  $18\text{ e}^-$  complexes, the inert gas configuration of latter is preserved as a result of substitution of one electron donor (halide, alkyl etc) by a bent nitrosyl or more generally  $n$ , two electron donors by  $\frac{2n}{3}\text{ NO}$ , groups. A few of the examples are



(M = Mo, W)

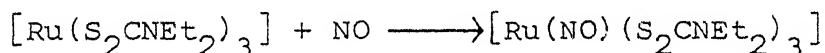
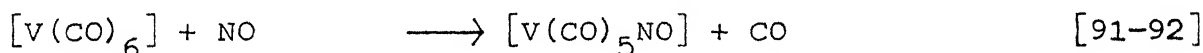
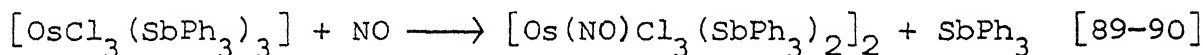


However in some of the cases introduction of NO group may not lead to an inert gas configuration. Thus, in the following examples fourteen electron system is going into fifteen electron one,



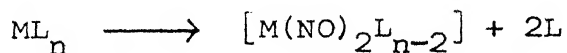
(chel = dithiocarbamate, dimethylglyoxime, schiffs base or porphyrin)

In case, the precursor complex is short of one electron from the inert gas configuration, the extra electron is achieved by substituting one two electron donor ligand by NO which will act as three electron donor,

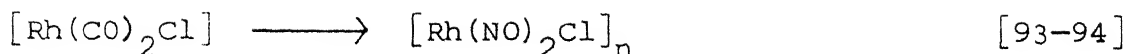


(one dithiocarbamate is monodentate)

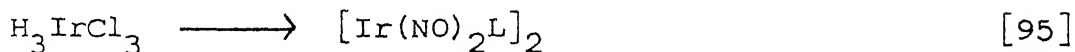
Reaction pattern becomes complicated when precursor metal complex is short of an even number of electrons (usually two) from the inert gas configuration. Under these circumstances two nitrosyl groups may substitute two ligand molecules producing a coordinatively saturated species,



The above behaviour accounts for the following reactions.



Substitution of one electron donor such as hydrogen may by NO results in the formation of metal-metal bond.

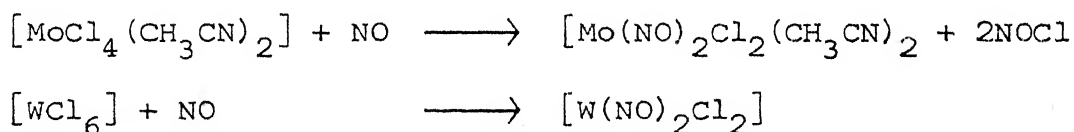


The dimer, having no bridging groups has Ir-Ir bond (2.717<sup>0</sup>Å).

The reaction of NO, with a coordinatively unsaturated complex often results in a redox reaction sometimes reducing the metal, while the remaining times disproportionation of NO, takes place.

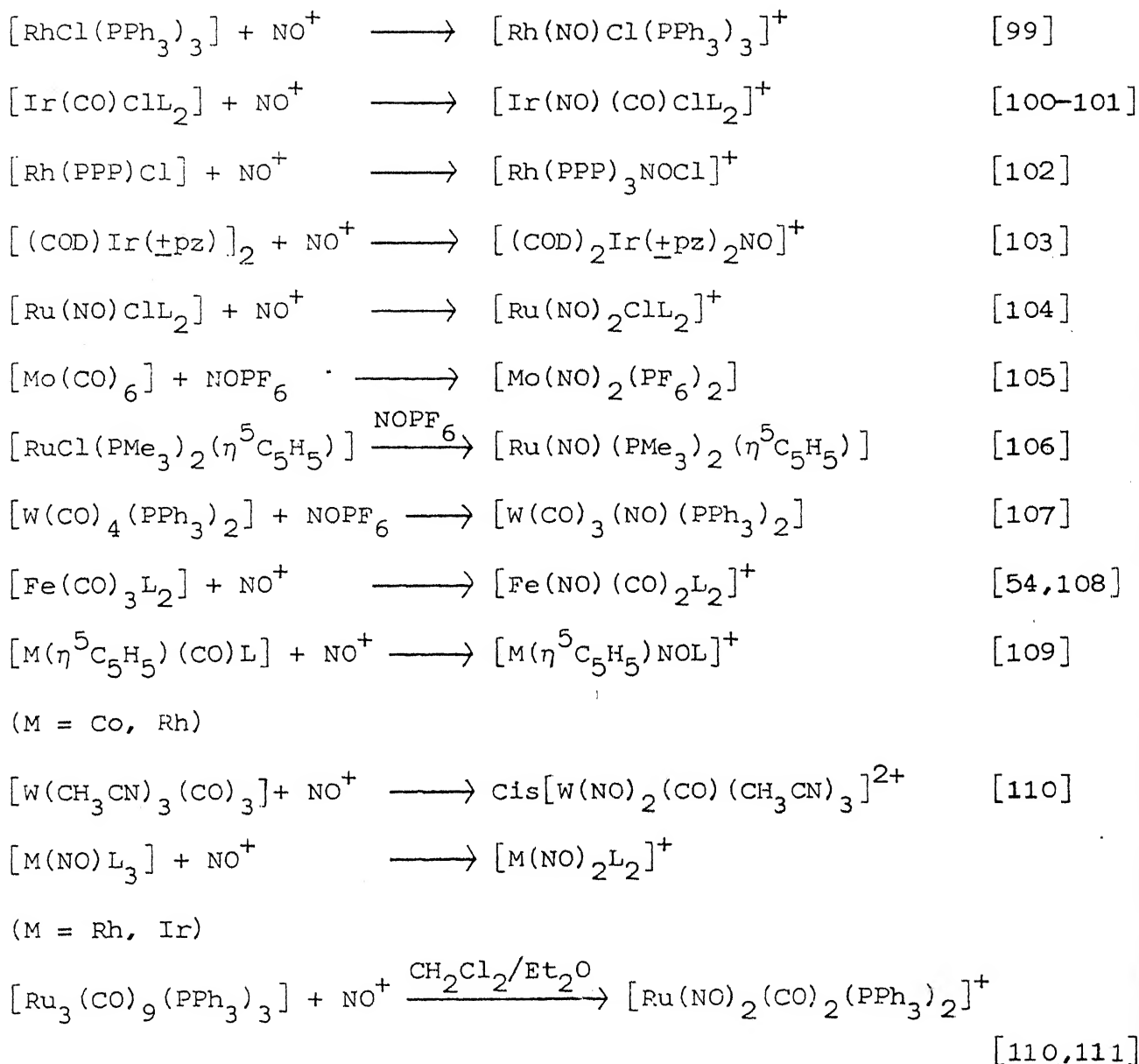
#### A.1(c) Reductive nitrosylation

Nitric oxide with an electron in its  $\pi$  orbital sometimes functions as a reducing agent during nitrosylation reaction. Higher halides of Mo and W are among several systems which undergo reductive nitrosylation [96-98]. Thus,



#### A.2 Nitrosonium ion ( $\text{NO}^+$ ) as nitrosylating agent

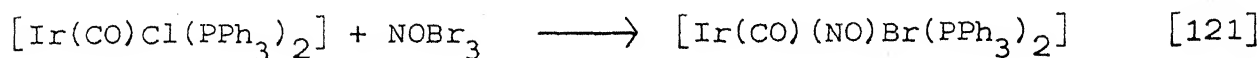
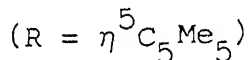
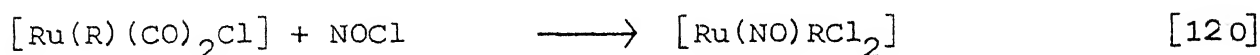
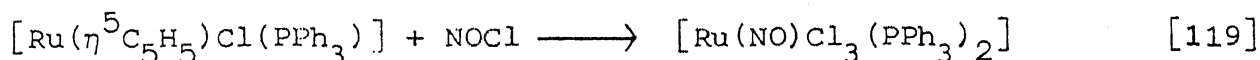
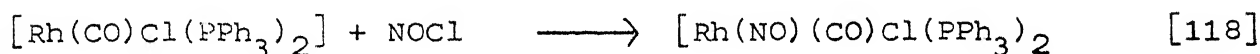
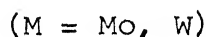
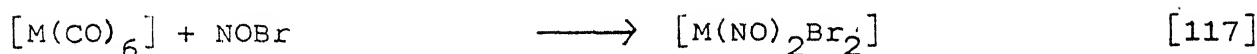
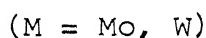
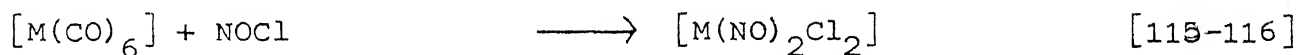
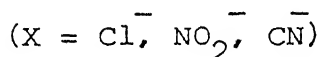
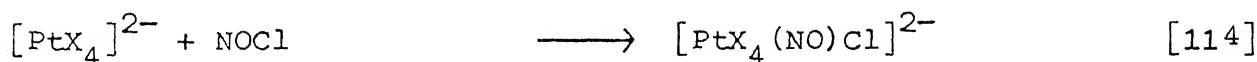
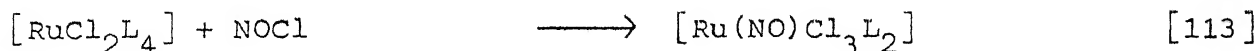
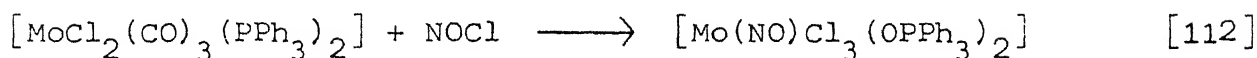
The salts of  $\text{NO}^+\text{X}^-$  ( $\text{X}^- = \text{BF}_4^-, \text{PF}_6^-, \text{HSO}_4^-$ ) provide excellent sources of  $\text{NO}^+$  in transition metal nitrosyl synthesis. Nitrosylation of metal ions with  $\text{NO}^+\text{X}^-$  may proceed either by the addition or by the substitution process. A few examples of these reactions are listed below;



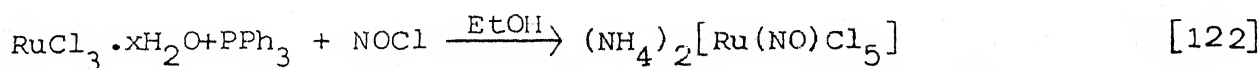
### A.3 NOX (X = Cl<sup>-</sup>, Br<sup>-</sup>, Br<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>) as nitrosylating agent

Oxidative addition of NOX with metal complexes in which the oxidation number of the central metal atom either remains the same after substituting the ligand molecules by NO and/or X or increases

by the addition of NO and X, has provided a potential synthetic procedure for many transition metal nitrosyls. Out of a large number of reactions a few are given below.

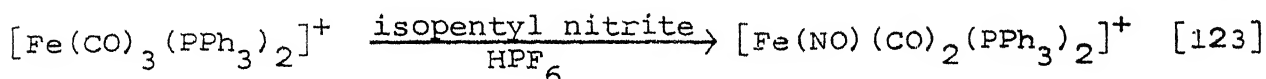


Recently a convenient route for the synthesis of the complex  $(\text{NH}_4)_2[\text{Ru}(\text{NO})\text{Cl}_5]$ , involving the reaction of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  with NOCl in presence of excess triphenylphosphine in alcoholic medium has been described.

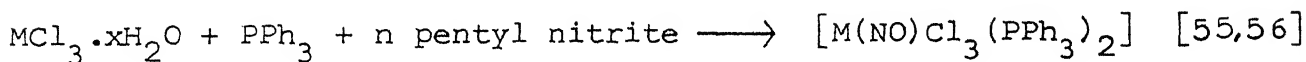


#### A.4 Alkyl nitrites as a source of nitrosyls

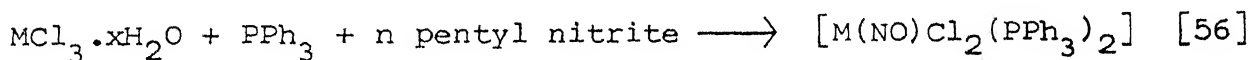
A study of the synthetic nitrosylating reactions indicate that the potential of alkyl nitrites for introducing NO in metal complexes has been utilized only in a few cases [51-56]. It therefore needs more extensive studies. A few known examples of such reactions include;



Metal chlorides of group VIII react in alcoholic medium to yield the corresponding nitrosyls,

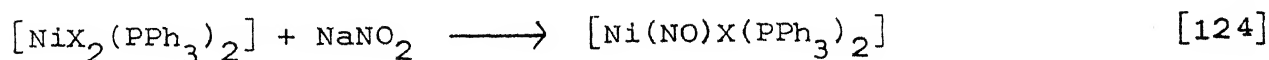


(M = Ru, Os)

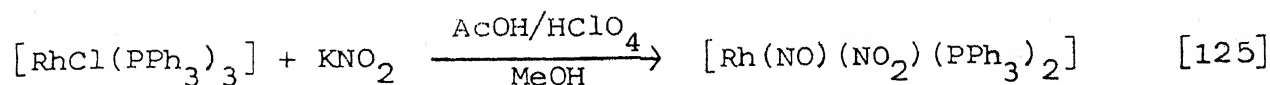


(M = Rh, Ir)

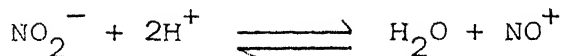
$\text{NaNO}_2$  and  $\text{KNO}_2$  have also been utilized in metal nitrosylation reactions,



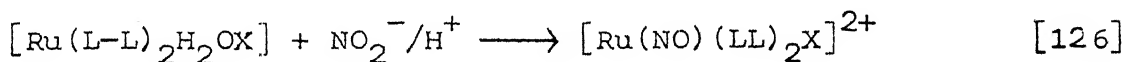
(X =  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_2^-$ )



The equilibrium reaction, underlying the method is given below,

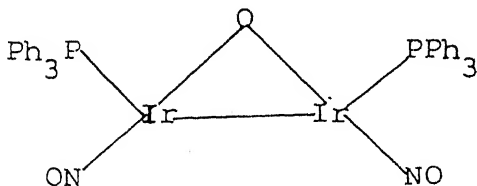


Godwin and Meyer [125] have successfully distinguished between the above reaction (attack of  $\text{NO}^+$  generated by acidic solution of nitrite salt on metal complex) from coordination of  $\text{NO}_2^-$ , followed by oxygen abstraction according to the following pathway.

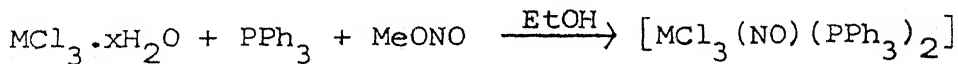


(L-L = 1,10-phenanthroline, 2,2'-bipyridyl)

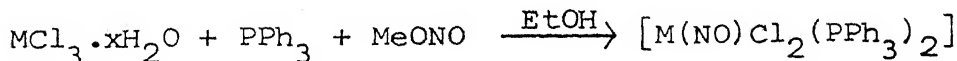
Vaska's complex interacts with  $\text{NaNO}_2$  in benzene/alcohol to yield  $[\text{Ir}(\text{NO})(\text{PPh}_3)]_2\text{O}$ , which possibly has a metal-metal bond [127].



Khan, et al. [57] have used methyl, ethyl, propyl and n-butyl nitrite for preparing metal nitrosyls in alcoholic medium.



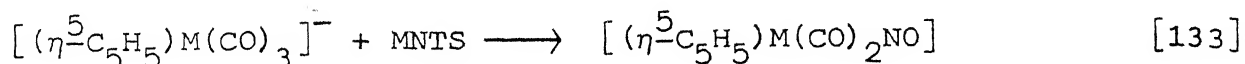
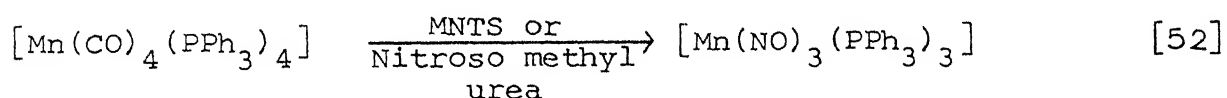
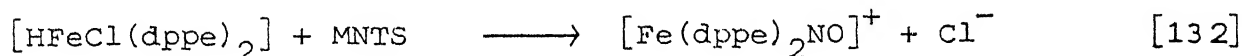
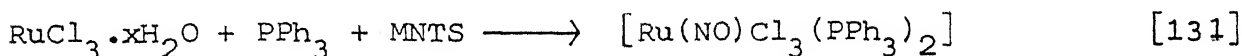
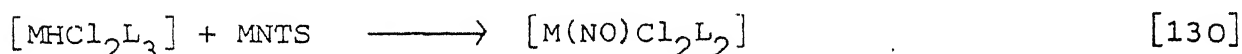
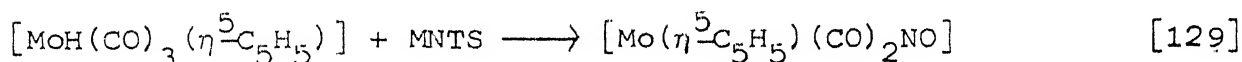
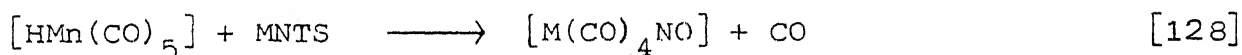
(M = Ru, Os)



(M = Rh, Ir)

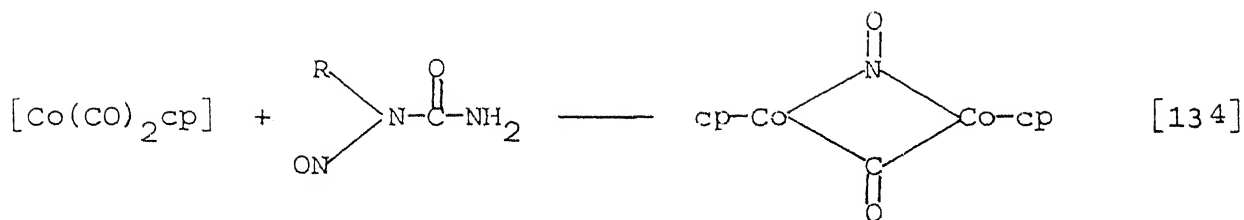
### A.5 N-nitrosamides as nitrosylating agent

N-nitrosamides such as N-methyl-N-nitroso urea, N-nitroso N-methyl-p-toluene sulphonamide react with a large number of metal hydrides to yield metal nitrosyls. In these reactions a hydrogen atom is substituted by nitrosyl group. Though it is expected that a bent nitrosyl complex will be the reaction product, it is, however, consistently found that the extrusion of a two electron donor ligand accompanies these reactions with the formation of linear nitrosyl complexes. Thus,

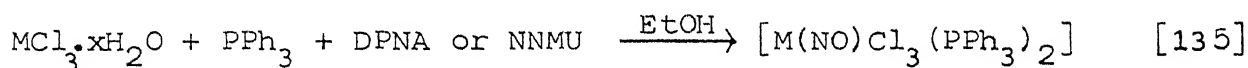


(M = Cr, Mo, W)

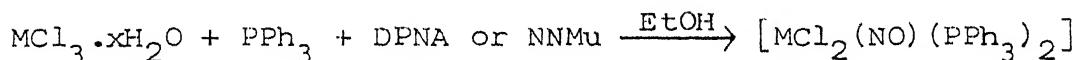
Interestingly, N-nitrosoalkyl urea reacts with  $[\text{Co}(\text{CO})_2\text{cp}]$  to yield a complex having one CO and one NO bridge between two metal centres.



Khan, et al. [135] have used N-nitroso-N-methyl aniline, diphenylnitrosamine, N-dibenzyl nitrosamine, N-nitroso N-phenyl benzylamine, N-nitroso-N-methyl urathane, N-nitrosodiethylcynamide and N-nitroso-N-methyl aminopyridine for preparing a variety of metal nitrosyl complexes in alcoholic medium.

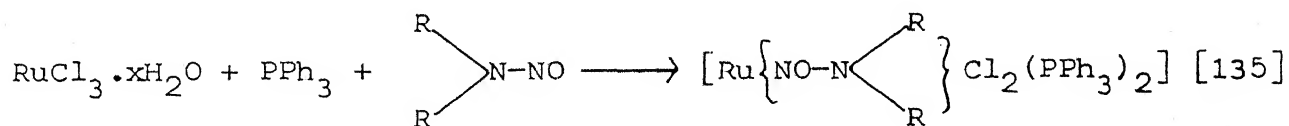


(M = Ru, Os)

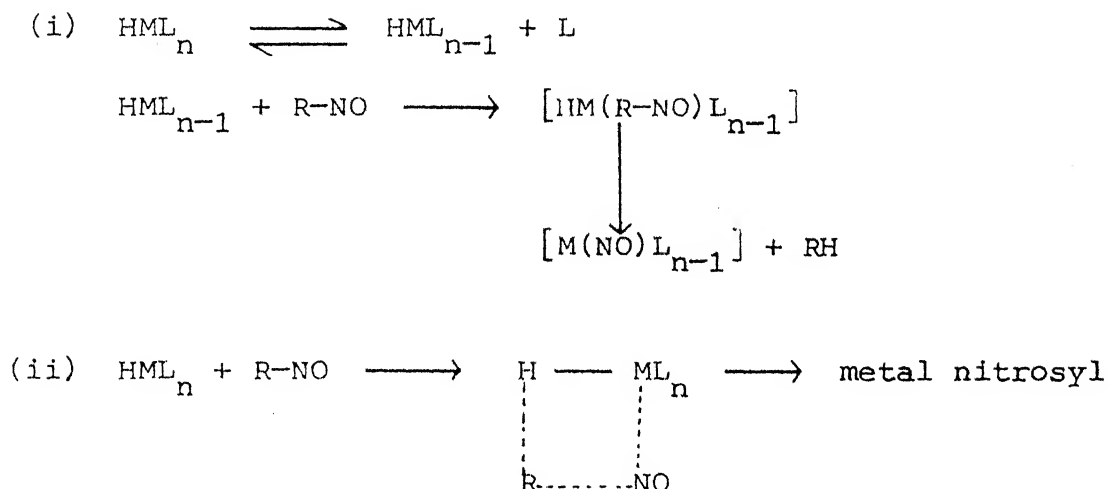


(M = Rh, Ir)

N-nitroso compounds with electron donating groups, like dimethylnitrosamine or diethylnitrosamine have not been found to be very effective nitrosylating agents. Instead they prefer to coordinate to the metal ions through N-atom because of the increased electron density on the N atom attached to the NO group.

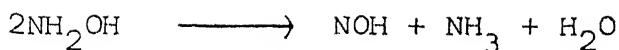


Following two different reaction mechanisms have been proposed for the nitrosylation reactions using nitrosamides.



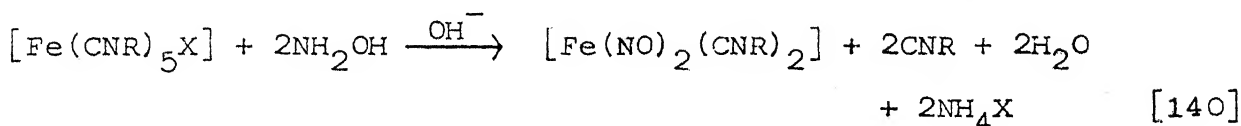
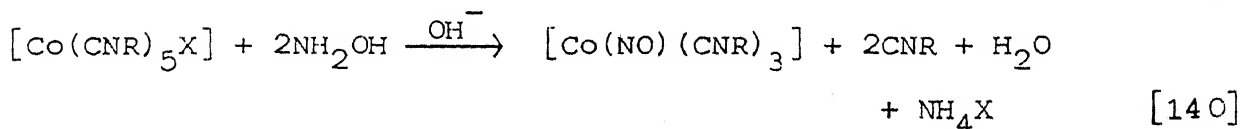
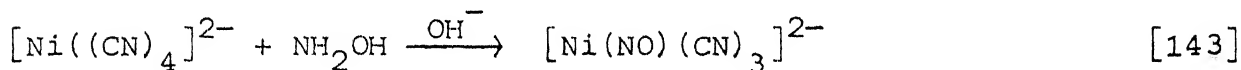
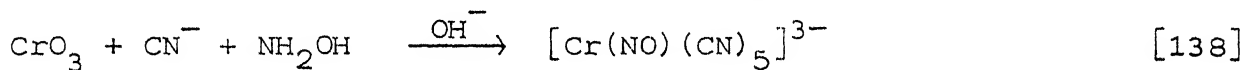
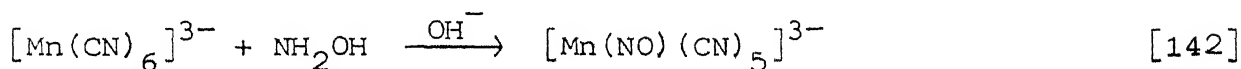
#### A.6 Hydroxylamine as a source of NO

Heiber, et al. [136,137] and Wilkinson and his coworkers [138,139] have successfully utilized hydroxylamine as nitrosylating agent in the synthesis of transition metal nitrosyls under strongly alkaline/cyanide medium. Wilkinson, et al. have synthesized  $\text{K}_3[\text{Cr}(\text{NO})(\text{CN})_5] \cdot \text{H}_2\text{O}$  using  $\text{CrO}_4^{2-}$  and  $\text{VO}_4^{2-}$ , respectively as reactants. The procedure has mainly been utilized in the synthesis of cyano complexes. Strongly alkaline medium was found to be necessary for activating the nitrosyl group because of the following reasons [136,140].

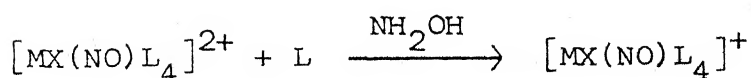


$\text{NO}^-$ , thus generated, acts as a reductive nitrosylating species.

Depending upon the pH,  $\text{NH}_2\text{OH}$  may generate  $\text{NH}_3$ ,  $\text{NH}_4^+$ ,  $\text{N}_2$  or  $\text{N}_2\text{O}$  [141]. A few of the reactions in which  $\text{NH}_2\text{OH}$  has been used as a nitrosylating agent are given below.



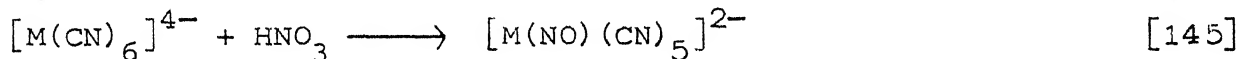
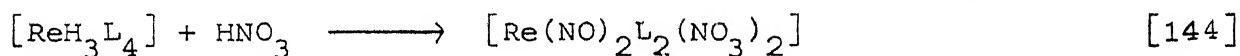
It is interesting to note that it can be used as nitrosylating agent in alkaline, neutral as well as in acidic medium. Compounds synthesized from  $\text{NH}_2\text{OH}$  under acidic, neutral or alkaline conditions have invariably linear M-NO, group. This has been confirmed by X-ray crystal structure data.



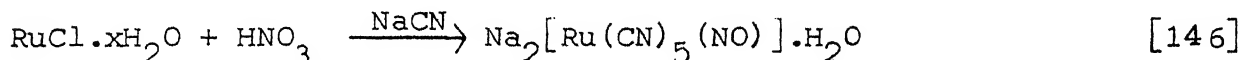
It is the first reaction to generate  $[\text{M-NO}]^{2+}$  group.

### A.7 Nitric acid as nitrosylating agent

Concentrated nitric acid has been employed in the synthesis of nitrosyl complexes preferentially in high oxidation states. The identity of the nitrosylating species during the course of reaction is still obscure. Probably the nitrosylation reaction proceeds via oxidative addition of  $\text{NO}^+\text{NO}_3^-$ . A few of the following examples support this view:

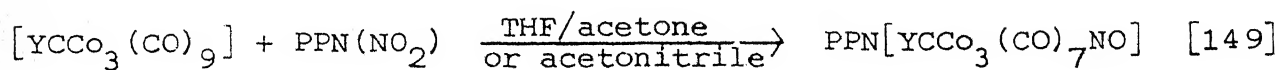


(M = Fe, Ru, Os)

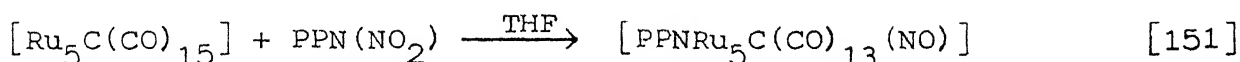
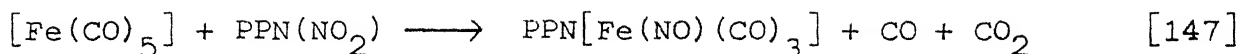
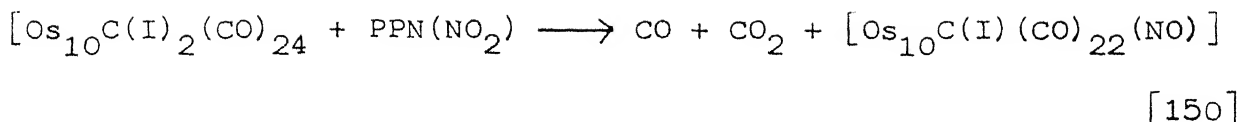


### A.8 Bis(triphenylphosphine)nitrogen (+1) nitrite $[\text{PPN}(\text{NO}_2)]$ as a nitrosylating agent

Bis(triphenylphosphine)nitrogen (+1) nitrite has recently been found as a new versatile nitrosylating agent for the metal carbonyl complexes [147-148]. Introduction of NO is generally accompanied by the loss of  $\text{CO}_2$ .  $\text{PPN}(\text{NO}_2)$  has commonly been used for preparing nitrosyl clusters.

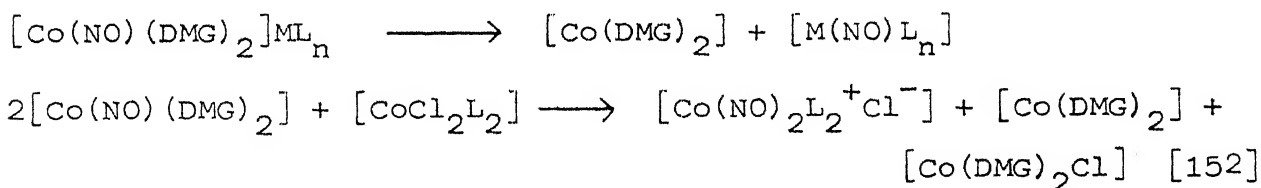


(Y = Me, Ph, COOH,  $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)$ )

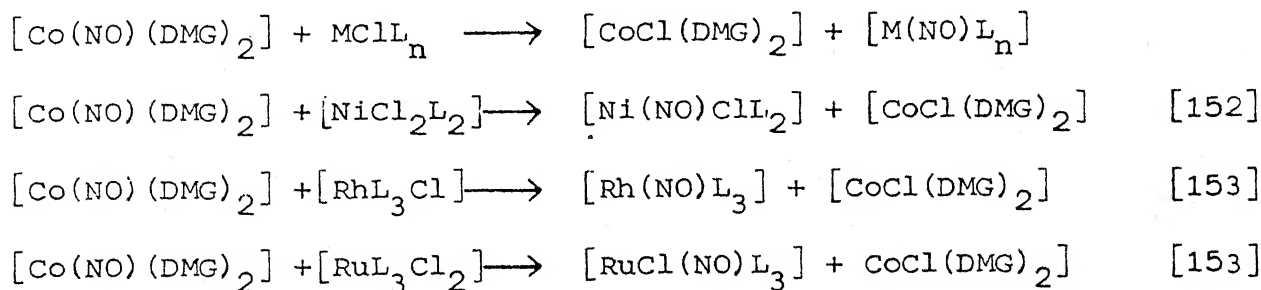


#### A.9 Transition metal nitrosyls as nitrosylating agents

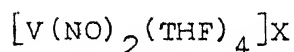
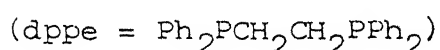
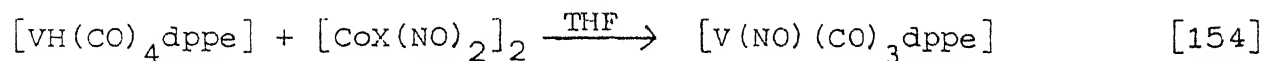
A few of the transition metal nitrosyls have successfully been utilized in the synthesis of the other transition metal nitrosyls.  $[\text{Co}(\text{NO})(\text{DMG})_2]$  with excellent solubility properties have been proved to be a potential transfer nitrosating agent in a number of reactions. The reaction of  $[\text{Co}(\text{NO})(\text{DMG})_2]$  with metal complexes can follow two path ways [152] (I) simple nitrosyl transfer. The following are the examples,



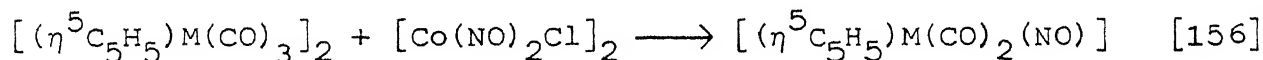
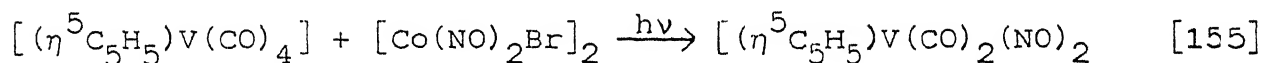
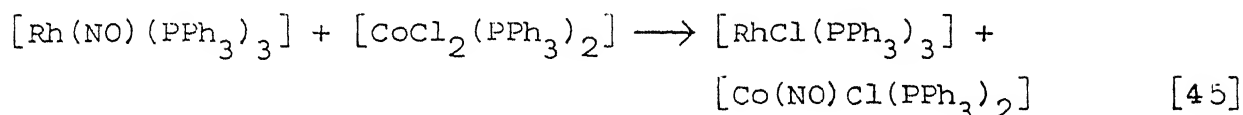
and (II) nitrosyl/halogen interchange or redistribution reaction,



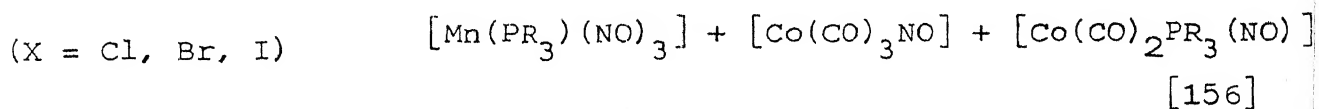
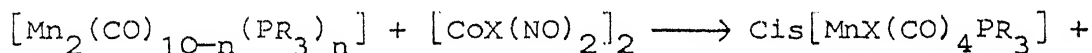
$[\text{Co}(\text{NO})_2\text{X}]_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) reacts with carbonyl hydrido phosphine vanadium complex to yield  $[\text{V}(\text{NO})_2(\text{THF})_4]\text{X}$  and  $[\text{V}(\text{CO})_3(\text{NO})(\text{dppe})]$  in dark.



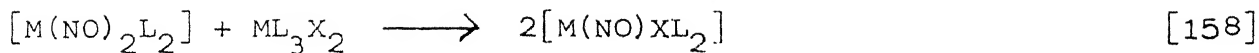
Some other representative reactions, where coordinated nitrosyl group of one complex has been used for the transfer nitrosation reaction, are:



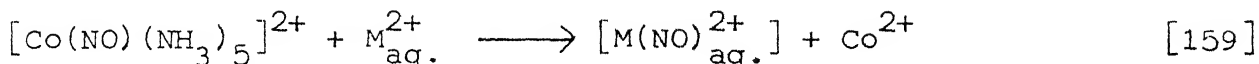
( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ )



Following examples clearly indicate that the nitrosyl transfer reactions are not limited to only  $[\text{Co}(\text{NO})(\text{DMG})_2]$ ,  $[\text{Co}(\text{NO})_2\text{X}]$  and  $[\text{Rh}(\text{NO})(\text{PPh}_3)_3]$ , but it also takes place using other metal nitrosyls.



(M = Ru, Os)



(M = Cr, Fe)

Summarily one may conclude that the nitrosation reaction using metal nitrosyls as nitrosylating agents takes place when the nitrosyl acceptor is coordinatively unsaturated.

#### I.2B Reactivity of transition metal nitrosyls

NO molecule has 15 electrons and is a stable free radical. It can readily be oxidised to  $NO^+$  but, the reduction of NO to yield  $NO^-$  does not proceed in a simple fashion. Instead, a dimeric species  $N_2O_2^{2-}$  is formed. Attempts have been made to correlate properties of nitrosyl complexes with the charge assigned to the coordinated NO group. Most commonly used criterion to determine the charge on NO has been the position of ( $\nu_{NO}$ ) in the i.r. spectra. A better criterion is the stereochemistry of M-NO grouping. In principle, there are three special cases where M-NO bond angle can be specified. These are: when the hybridization of nitrogen atom is  $sp$ ,  $sp^2$  and  $sp^3$ . In case, the conventional ligand field premise is followed, the NO has a charge of +1 when  $sp$ , hybridized, of -1 when  $sp^3$  hybridized and zero when  $sp^2$  hybridized. As has been cited previously, it functions both as an electron donor ( $NO^+$ ) or as an electron acceptor ( $NO^-$ ), depending on the

nature of the metal ions. In some cases the bonding may be as  $\text{N}_2\text{O}_2^{2-}$ . Consequently, the bonding mode determines the partial charge, that develops on the nitrogen and the oxygen atom of the bonded NO group resulting in the interesting variation in its reactivity [69]. It has, thus, been demonstrated that the complexes with linear M-NO (charge +1) and with  $(\nu_{\text{NO}})$  usually greater than  $1850\text{ cm}^{-1}$  undergo nucleophilic reactions, while, those with bent M-NO (charge -1), electrophilic reactions [160]. Another reason for investigating the reactivity of the coordinated NO group largely stems from the attempts to remove, or atleast diminish the concentration of NO in the exhaust gases emitted by the internal combustion engines, which has an important bearing on pollution control. Furthermore, there exists a definite possibility of forming organo-nitrogen compounds using nitric oxide in reactions assisted or moderated by transition metal catalysts. Tables I.1 through I.5 summarize the results of the reactions of metal nitrosyls with nucleophiles ( $\text{OH}^-$ ,  $\text{N}_3^-$ ,  $\text{NCO}^-$ ,  $\text{OEt}^-$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{H}_4$ ,  $\text{NH}_2\text{OH}$ ,  $\text{ArNH}_2$ , etc) and electrophiles ( $\text{HCl}$ ,  $\text{PhCH}_2\text{Br}$ ,  $\text{O}_2$  etc.). The results of the reduction insertion and other reactions undergone by the transition metal nitrosyls specially those of ruthenium, rhodium, iridium, cobalt, molybdenum and tungston are described therein.

Table I.1. Reactions of the nitrosyl complexes of ruthenium

Reactant	Reagent	Product	Notes	Reference
1	2	3	4	5
1. $[\text{Ru}(\text{NO})\text{Cl}(\text{Bipy})_2]^{2+}$	$\text{OH}^-$	$[\text{Ru}(\text{NO}_2)\text{Cl}(\text{Bipy})_2]^{2+}$	Bipy = 2,2'-bipyridine	126
2. $[\text{Ru}(\text{NO})\text{Cl}(\text{Bipy})_2]^{2+}$	$\text{ArNH}_2$	$[\text{RuCl}(\text{Bipy})_2(\text{NNAr})]^{2+}$	Ar = p- $\text{RC}_6\text{H}_4$ ; R = H, $\text{CH}_3$ or $\text{CH}_3\text{O}$	161
3. $[\text{Ru}(\text{NO})\text{Cl}(\text{Bipy})_2]$	$\text{C}_6\text{H}_5\text{NRMe}$	$[\text{RuCl}(\text{Bipy})_2^- \text{N}(=\text{O})\text{C}_6\text{H}_4\text{NRMe}]^+$		162
4. $[\text{Ru}(\text{NO})\text{Cl}(\text{Bipy})_2]$	$\text{N}_3^-$	$[\text{RuCl}(\text{Bipy})_2(\text{H}_2\text{O})]^{2+} + \text{N}_2 + \text{H}_2\text{O}$		163
5. $[\text{Ru}(\text{NO})\text{Cl}(\text{Bipy})_2]$	$\text{NH}_3$	$[\text{Ru}(\text{NO}_2)\text{Cl}(\text{Bipy})_2]^{2+}$		126
6. $[\text{Ru}(\text{NO})\text{Cl}(\text{diars})_2]^{2+}$	$\text{OH}^-$	$[\text{Ru}(\text{diars})_2\text{Cl}(\text{NO}_2)]^{2+}$		164
7. $[\text{Ru}(\text{NO})\text{Cl}(\text{diars})_2]^{2+}$	$\text{N}_3^-$	$[\text{Ru}(\text{diars})_2\text{Cl}(\text{N}_3)]^{2+} + \text{N}_2\text{O} + \text{N}_2$	The intermediate involved in the reaction has been proposed to bound to metal either as	165
			$\left[ \text{Ru}-\text{N} \begin{array}{c} \text{O} \\ \parallel \end{array} \text{N}=\text{N}^+=\text{N} \right]^+ \quad \text{or} \quad \text{Ru}-\text{N} \begin{array}{c} \text{O} \\ \diagup \end{array} \text{N} \begin{array}{c} \diagdown \end{array} \text{N} \end{array}$	
8. $[\text{Ru}(\text{NO})\text{Cl}(\text{diars})_2]^{2+}$	$\text{N}_2\text{H}_4$	$[\text{RuCl}(\text{N}_3)(\text{diars})_2]$		164
9. $[\text{Ru}(\text{NO})\text{Cl}(\text{diars})_2]^{2+}$	$\text{PhNHNH}_2$	$[\text{RuCl}(\text{diars})_2\text{N}(\text{O})\text{NNHPh}]$		164

...contd.

Table I.1(contd.)

1	2	3	4	5
10. $[\text{Ru}(\text{NO})\text{Cl}(\text{diars})_2]^{2+}$	$\text{NH}_3$	$[\text{Ru}(\text{NO}_2)\text{Cl}(\text{diars})_2]^{2+}$		164
11. $[\text{Ru}(\text{NO})(\text{CN})_5]^{2-}$	$\text{OH}^-$	$[\text{Ru}(\text{NO}_2)(\text{CN})_5]^{4-}$		71
12. $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$	$\text{OH}^-$	$[\text{Ru}(\text{NH}_2)(\text{NH}_3)_4(\text{NO})]^{2+}$ + $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ or $[\text{Ru}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ or $[\text{Ru}(\text{NH}_3)_5(\text{NO})(\text{OH})]^{2+}$	Product are $\text{OH}^-$ concentration dependent	166
13. $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$	$\text{RNH}_2$	$[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+} + \text{ROH}$	R = Me or Et Reaction occurs at pH = 10	167
14. $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$	$\text{NH}_3$	$[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})]^{2+} + \text{N}_2\text{O} + \text{N}_2$ or $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$		71
15. $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$	$\text{N}_2\text{H}_4$	$[\text{Ru}(\text{NH}_3)_5(\text{N}_2\text{O})]^{2+}$ and/or $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+} + [\text{Ru}(\text{NH}_3)_5(\text{N}_3)]^{2+}$	Product, temperature dependent	168
16. $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$	$\text{NH}_2\text{OH}$	$[\text{Ru}(\text{NH}_3)_5(\text{N}_2\text{O})]^{2+} + \text{N}_2\text{O} + \text{N}_2$		169
17. $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2]$	HCl	$[\text{RuH}(\text{NO})_2(\text{PPh}_3)_2]^+$ — $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$	In the absence of oxygen	168

...contd.

Table I.1(contd.)

1	2	3	4	5
18. $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2]$	$\text{PhCH}_2\text{Br}$	$[\text{Ru}(\text{CO})(\text{NO})\text{Br}(\text{PPh}_3)_2]$ and/or $[\text{RuBr}_2(\text{CO})_2(\text{PPh}_3)_2] + \text{PhCN}$ + $\text{PhCONH}_2 + \text{PhCN}=\text{NOH}$	At 110°C temperature and under CO atmos- phere in toluene	170
19. $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2]$	$\text{O}_2$	$[\text{Ru}(\text{NO})(\text{NO}_3)(\text{O}_2)(\text{PPh}_3)_2]$ or $[\text{Ru}(\text{NO})_2(\text{OH})(\text{PPh}_3)_2]^+$	In absence of acid	168
20. $[\text{Ru}(\text{CO})(\text{NO})\text{X}(\text{PPh}_3)_2]$	$\text{O}_2$	$[\text{Ru}(\text{NO})(\text{O}_2)(\text{PPh}_3)_2\text{X}]$	In presence of acid X = Cl or NCS	1
21. $[\text{Ru}(\text{NO})(\text{O}_2)(\text{NCS})(\text{PPh}_3)_2]$	$2\text{PPh}_3$	$[\text{Ru}(\text{NO})(\text{O}_2)(\text{NCS})(\text{PPh}_3)_2]$ + 2 $\text{O}=\text{PPh}_3$		171
22. $[\text{Ru}(\eta^3\text{-C}_3\text{H}_5)(\text{NO})(\text{PPh}_3)_2]$	CO	$[\text{Ru}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})(\text{NO})(\text{PPh}_3)_2]$ + $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2] + \text{acrolein}$ oxime		172
23. $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$	$e^-$	$[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{2+}$	Reversible reaction	173
24. $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$	$\text{Cr}^{2+} + \text{H}^+$ + $\text{H}_2\text{O}$	$[\text{Ru}(\text{NH}_3)_6]^{2+}$		160
25. $[\text{Ru}(\text{NO})\text{Cl}_5]^{2-}$	Alk. HCHO	$[\text{Ru}_2\text{N}(\text{OH})_5(\text{H}_2\text{O})_5] \cdot n\text{H}_2\text{O}$		174
26. $[\text{Ru}(\text{NO})\text{Cl}_5]^{2-}$	$\text{SnCl}_2/\text{HCl}$	$[\text{Ru}_2\text{Cl}_8\text{N}(\text{H}_2\text{O})_2]^{3-}$		175

...contd.

Table I.1(contd.)

1	2	3	4	5
27. $[\text{Ru}(\text{OH})(\text{NO})_2]_4(\text{NO})^{2-}$	$2\text{OH}^-$	$[\text{Ru}(\text{OH})(\text{NO})_2]_5^{4-} + \text{H}_2\text{O}$		69
28. $[\text{Ru}(\text{NO})\text{X}_5]^{2-}$	$h\nu, \text{H}_2\text{O}$	$[\text{Ru}(\text{H}_2\text{O})\text{X}_5]^{2-} + \text{NO}$	Photolysis in aq. solution, X = Cl, Br or I, reversible reaction	176
29. $[\text{Ru}(\text{NO})\text{Cl}(\text{Bipy})_2]^{2+}$	$h\nu, \text{CH}_3\text{CN}$	$[\text{RuCl}(\text{CH}_3\text{CN})(\text{Bipy})_2]^{2+} + \text{NO}$	Reversible reaction, photo- lysis in $\text{CH}_3\text{CN}$ medium	176
30. $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2\text{Cl}]^+$	$\text{Cl}^-$	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$	Excess $\text{Cl}^-$ ions; Fate of NO is not known	177
31. $[\text{Ru}(\text{NO})\text{Cl}(\text{O}_2)(\text{PPh}_3)_2]$	$2\text{CO}$	$[\text{Ru}(\text{NO}_3)(\text{CO})_2\text{Cl}(\text{PPh}_3)_2]$		178
32. $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2]$	$h\nu, \text{CO}$	$[\text{Ru}(\text{CO})_4(\text{PPh}_3)_2] + \text{CO}_2$ + $\text{N}_2\text{O}$	24 hours reaction under 100 atmosphere in presence of CO	7
33. $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$	$\text{PPh}_3$	$[\text{Ru}_4(\mu\text{-PPh}_2)_4(\mu\text{-Cl})_4(\text{NO})_4]$	In reduction condition	179
34. $[\text{Ru}(\text{NO})\text{Cl}_3(\text{H}_2\text{O})]$	Glycine (gly)	$\text{K}[\text{Ru}(\text{gly})(\text{OH})_3(\text{NO})]$		180
35. $[\text{Ru}(\text{NO})(\text{NO}_3)_x]^{(3-x)+}$ • $\text{YH}_2\text{O}$	2,2'- Bipy	$[\text{Ru}(\text{NO})(\text{NO}_3)_z]^{(3-z)+}$ and $[\text{Ru}(\text{NO})(\text{bpy})_2\text{NO}_3]^{2+}$	2,2'-Bipy = 2,2'-Bipyridine in presence of aq. $\text{HNO}_3$ absence of reducing agent	181
36. $[\text{Ru}(\text{NO})(\text{NO}_3)_x]^{(3-x)+}$ • $\text{YH}_2\text{O}$	2,2'- Bipy	$[\text{Ru}(\text{NO})(\text{bpy})(\text{NO}_3)]^{2+}$ + $[\text{Ru}(\text{NO})(\text{bpy})_2\text{NO}_3]^{2+}$	In presence of reducing agent	181

...contd.

Table I.1 (contd.)

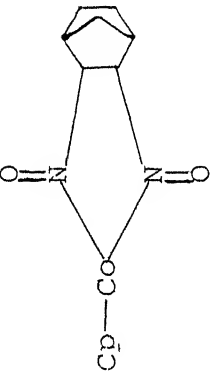
1	2	3	4	5
37. $\text{Na}_2\text{Ru}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{OH}^-, \text{SH}^-, \text{SO}_3^{2-},$ $\text{NH}_3, \text{N}_2\text{H}_4$	$[\text{Ru}(\text{CN})_5\text{H}_2\text{O}]^{3-}$		146
8. $[\text{RuX}(\text{NO})\text{L}_4]^{2+}$	$\text{NH}_2\text{OH}$	$[\text{RuX}(\text{NO})\text{L}_4]^{+}$	X = Cl or Br L = Pyridine or O-phenyl- enebis(dimethylarsine)	182
39. $[\text{Ru}_3(\text{CO})_{10}(\mu_2\text{-NO})_2]$	CO, 1 atm 110°C	$[\text{Ru}_3(\text{CO})_{12}]$ , $\text{Ru}_3(\text{CO})_{10}(\mu_2\text{-NO})$ , ( $\mu_2\text{-NCO}$ ), $[\text{Ru}_4\text{N}(\text{CO})_{12}\mu_2\text{-L}]$	Via the intermediate $[\text{Ru}_3\text{N}(\text{CO})_{10}\text{NO}]$	183
40. $[\text{RuCl}_5(\text{NO})]^{2-}$	HL	$[\text{RuCl}_2\text{L}_2(\text{NO})]$	HL = Pyridine-2-carboxylic acid	180
41. $[\text{Ru}(\text{NO})_2\text{L}_2]$	$\text{PhCH}_2\text{Br}$	$[\text{RuBr}(\text{CO})\text{NOL}_2]$ , $[\text{RuBr}_2(\text{CO})_2\text{L}_2]$ , PhCH: NOH, PhCN, BzNH <sub>2</sub> , PhCHO, PhCH <sub>2</sub> OH	L = PPh <sub>3</sub> under CO in refluxing PMe <sub>3</sub>	184
42. $[\text{Ru}(\text{NO})_2\text{L}_2]$	$\text{PhCH}_2\text{Br}$	$[\text{RuBr}_2(\text{NCPH})_2\text{L}_2]$ , $[\text{RuBr}_3(\text{NO})\text{L}_2]$ , PhCN, BzNH <sub>2</sub> , PhCH <sub>2</sub> CH <sub>2</sub> Ph, PhCHO	In the absence of CO	184

Table I.2. Reactions of the nitrosyl complexes of cobalt

Reactant	1		Reagent	Product	Notes	Reference
	1	2				5
1. $[\text{Co}(\text{diars})_2(\text{NO})](\text{ClO}_4)_2$		HBr	$[\text{Co}(\text{diars})_2\text{Br}(\text{HNO})]^{2+}$		Br <sup>-</sup> acting as lewis base	185
2. $[\text{Co}(\text{NO})(\text{PPh}_3)_3]$		HCl	$[\text{Co}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ + $[\text{CoCl}_2(\text{PPh}_3)_2]$			20
3. $[\text{Co}(\text{NO})(\text{PPh}_3)_3]$		$\text{C}_6\text{H}_5\text{COCl}$	$[\text{Co}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ + $\text{C}_6\text{H}_5\text{Cl} + \text{PPh}_3$			23
4. $[\text{Co}(\text{NH}_3)_5(\text{NO})]^{2+}$		$\text{Cr}^{2+}$	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+} + \text{NO}$			160
5. $[\text{Co}(\text{NO})_2(\text{PPh}_3)_2]$		$\text{BH}_4^-$	$[\text{Co}(\text{NO})(\text{PPh}_3)_3] + \text{NH}_3$			175
6. $\text{cis}-[\text{Co}(\text{en})_2(\text{NO})-(\text{MeOH})]\text{Cl}_2$		NO	$\text{cis}-[\text{CoCl}(\text{NO}_2)(\text{en})_2]\text{Cl}$ + $\text{N}_2\text{O}$	In MeOH		186
7. $[\text{Co}(\text{NO})(\text{PPh}_3)_3]$		7 NO	$[\text{Co}(\text{NO})_2(\text{NO}_2)(\text{PPh}_3)]$ + $2 \text{O} = \text{PPh}_3 + 2\text{N}_2\text{O} + \frac{1}{2} \text{N}_2$			187
8. $[\text{Co}(\text{NO})(\text{CO})_3]$		NO	$[\text{Co}(\text{N}_3\text{O}_4)]_n + [\text{Co}_4(\text{NO})_8]^-$ $(\text{NO}_2)_3(\text{N}_2\text{O}_2)]$	$n = \infty$ in solid; $n = 2$ in solution		188

...contd.

Table I.2(contd.)

1	2	3	4	5
9. $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(-\text{NO})]_2$	Norbornene		In NO atmosphere $\text{C}_p = (\eta^5\text{-C}_5\text{H}_5)$	189
10. $[\text{Co}(\text{NO})(\text{DMG})_2]$	$[\text{RhCl}(\text{PPh}_3)_3]$	$[\text{Rh}(\text{NO})(\text{PPh}_3)_3] + [\text{Rh}(\text{NO})-\text{Cl}_2(\text{PPh}_3)_2 + [\text{CoCl}(\text{MDG})_2\text{L}]$	L = Lewis base associated with the reagent	33
11. $[\text{Co}(\text{NO})(\text{MDG})_2]$	$[\text{Rh}(\text{CO})-(\text{PPh}_3)_3]$	$[\text{Rh}(\text{CO})(\text{NO})(\text{PPh}_3)_2] + [\text{Rh}(\text{NO})(\text{PPh}_3)_3] \text{ (trace amount)} + [\text{CoCl}(\text{DMG})_2\text{L}]$	L = Lewis base associated with the reagent	33
12. $[\text{Co}(\text{NO})(\text{diars})_2]^{2+}$	NCS <sup>-</sup>	$[\text{Co}(\text{NO})(\text{diars})_2(\text{NCS})]^+$		190
13. $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{NO})]^{2-}$	Na/Hg	$\text{Na}^+[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{NO})]^-$ $\xrightarrow[\text{MeI}]{\text{THF}} (\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{Me})(\text{NO})$	In Et <sub>2</sub> O	191
14. $[\text{Co}(\text{CO})_3\text{NO}]$	$\text{CH}_2\text{CHCHCH}_2$ , (C <sub>4</sub> H <sub>6</sub> ), UV radiation	trans $\eta^2\text{-C}_4\text{H}_6\text{Co}(\text{CO})_2\text{NO}$ cis $\eta^4\text{-C}_4\text{H}_6\text{Co}(\text{CO})\text{NO}$	In ligand xenon solution	192

...contd.

Table I.2(contd.)

1	2	3	4	5
15. $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{2+}$	$\text{Cr}^{2+}$	$\text{Co}^{2+} + [\text{CrONO}(\text{H}_2\text{O})_5]^{2+}$		193
16. $[\text{cpCo}(\mu_2\text{NO})]_2$	NHR	$[\text{cp}_2\text{Co}_2(\mu_2\text{-NO})(\mu_2\text{-NHR})]$	R = t C <sub>4</sub> H <sub>8</sub>	34

Table I.4. Reactions of the nitrosyl complexes of iridium

Reactant	Reagent	Product	Notes	Reference
1	2	3	4	5
1. $[\text{Ir}(\text{NO})\text{X}_5]^{2-}$	$\text{OH}^-$	$[\text{Ir}(\text{NO}_2)\text{X}_5]^{3-}$	X = Cl, Br	197
2. $[\text{Ir}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]^+$	$\text{OEt}^-$	$[\text{IrCl}_3\{\text{N}(\text{=O})\text{OEt}\}(\text{PPh}_3)_2]$		21
3. $[\text{Ir}(\text{NO})(\text{NCMe})_2(\text{PPh}_2)_3]^{2+}$	$\text{OH}^-$	$[\text{Ir}(\text{NO})(\text{OH})(\text{PPh}_3)_2]^+$		194
4. $[\text{Ir}(\text{NO})\text{X}_5]^{2-}$	$\text{NH}_3$	$[\text{Ir}(\text{NH}_3)\text{Cl}_5]^{2-} + \text{N}_2$	X = Cl, Br	197
5. $[\text{Ir}(\text{NO})\text{X}_5]^{2-}$	$\text{N}_3^-$	$[\text{IrCl}_5(\text{H}_2\text{O})]^{2-} + \text{N}_2 + \text{N}_2\text{O}$	Aqueous medium	197
6. $[\text{Ir}(\text{NO})\text{X}_5]^{2-}$	$\text{NH}_2\text{OH}$	$[\text{IrCl}_5(\text{H}_2\text{O})]^{2-} + \text{N}_2\text{O}$	Aqueous medium	197
7. $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$	HCl	$[\text{IrCl}_3(\text{NH}_2\text{OH})(\text{PPh}_3)_2]$	Excess HCl	20
		$\downarrow \text{CO}$		
		$[\text{Ir}(\text{CO})\text{Cl}_3(\text{PPh}_3)_2]$		
8. $[\text{Ir}(\text{NO})_2(\text{PPh}_3)_2]^+$	$\text{O}_2$	$[\text{Ir}(\text{NO})(\text{NO}_3)(\text{PPh}_3)_2]$		104
9. $[\text{IrBr}(\text{NO})_2(\text{PPh}_3)_2]$	$3(\text{CO})$	$[\text{IrBr}(\text{CO})_2(\text{PPh}_3)_2] + \text{CO}_2 + \text{N}_2\text{O}$		177
10. $[\text{Ir}(\text{CO})(\text{NO})(\text{PPh}_3)_2]$	$\text{PPh}_3$	$[\text{Ir}(\text{NCO})(\text{PPh}_3)_3]$	In presence of the UV light	7
11. $[\text{IrBr}(\text{NO})_2(\text{PPh}_3)_2]$	NO	$[\text{IrBr}(\text{NO})(\text{NO}_2)(\text{PPh}_3)_2] + \text{N}_2\text{O}$		177

...contd.

Table I.4(contd.)

1	2	3	4	5
12.	$[\text{Ir}(\text{CO})(\text{NO})\text{XCl}(\text{PPh}_3)_2]$ (X = Cl, Br, I, NCS, NCO, N <sub>3</sub> )	O <sub>2</sub>	$[\text{Ir}(\text{CO})(\text{NO}_3)\text{XCl}(\text{PPh}_3)_2]$	In C <sub>6</sub> H <sub>6</sub> at 25°C rate of reaction decreases with X as I > Br > Cl NCS > NCO > N <sub>3</sub>
13.	$[\text{Ir}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]^+$	ROH	$[\text{IrCl}_3(\text{PPh}_3)_2\text{N}(\text{O})\text{OR}]^+ + \text{H}^+$	21
14.	$[\text{Ir}(\text{NO})(\text{CH}_3\text{CN})_3(\text{PPh}_3)_2][\text{PF}_6]$ (dppn 3,6-bis- (2'-pyridyl)pyridazine)	dppn/CuCl <sub>2</sub> · ·xH <sub>2</sub> O	$[\text{IrCl}(\text{PPh}_3)_2(\mu\text{-dppn})(\mu\text{-NO})-$	198
15.	$[\text{Ir}(\text{NO})(\text{MeCN})_3(\text{PPh}_3)_2]^-$ [PF <sub>6</sub> ]	9,10- phenan- threnequ- inonedii- mine(H <sub>2</sub> L)	$[\text{Ir}(\text{NO})(\text{H}_2\text{L})(\text{PPh}_3)_2][\text{PF}_6]$	199
16.	$[\text{IrCl}(\text{NO})\text{L}_2]^+ (\text{L} = \text{PPh}_3)$	Tetra- allyltin	$[\text{Ir}(\text{NO})(\eta^3\text{-C}_3\text{H}_5)_2\text{L}_2]^+$	200
17.	$[(\text{COD})_2\text{Ir}_2(\mu\text{-pz})_2\text{NO}][\text{BF}_4]$	Co(g)	$[(\text{COD})_2\text{Ir}_2(\mu\text{-pz})_2(\text{NO})(\text{CO})][\text{BF}_4]$	103
18.	$[(\text{COD})_2\text{Ir}_2(\mu\text{-pz})_2\text{NO}][\text{BF}_4]$	HCl	$[(\text{COD})_2\text{Ir}_2(\mu\text{-pz})_2(\mu\text{-NO})\text{Cl}_2][\text{BF}_4]$	103

Table I.5. Reactions of a few nitrosyl complexes of molybdenum and tungstan

Reactant	Reagent	Product	Notes	Refe-
				rence
1	2	3	4	5
1. $[\text{Mo}(\text{NO})_2(\text{S}_2\text{CNET}_2)_2]$	$\text{N}_3^-$	$[\text{Mo}(\text{NO})(\text{S}_2\text{CNET}_2)_3] + \text{N}_2\text{O}$ + $[\text{Mo}(\text{NO})(\text{N}_3)(\text{DMSO}) -$ $(\text{S}_2\text{CNET}_2)_2]$	In DMSO	201
2. $[\text{Mo}(\text{NO})_2(\text{S}_2\text{CNET}_2)_2]$	$\text{NCO}^-$	$[\text{Mo}(\text{NO})(\text{S}_2\text{CNET}_2)_2] + [\text{Mo}(\text{NO}) -$ $(\text{NCO})(\text{DMSO})(\text{S}_2\text{CNET}_2)_2]$		201
3. $[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$	Heat (340- 350°C)	$[\text{MoOCl}_4] + \text{MoO}_2\text{Cl}_2 + \text{Mo} + \text{N}_2\text{O}$		202
4. 3 cis- $[\text{Mo}(\text{NO})_2(\text{S}_2\text{CNR}_2)_2]$	UV radia- tions	$2[\text{Mo}(\text{NO})(\text{S}_2\text{CNR}_2)_3] + 2 \text{N}_2\text{O}$ + $\text{MoO}_2$	On irradiation of the reactant the reaction proceeds via formation of a dimeric hyponi- trite intermediate- $[(\text{ON})(\text{R}_2\text{NCS}_2)_2\text{Mo}-$ $\text{N}(\text{O})\text{N}(\text{O})\text{Mo}(\text{S}_2-$ $\text{CNR}_2)_2(\text{NO})]$	203
5. $\text{K}_4[\text{Mo}(\text{NO})(\text{CN})_5]$	HCl/cscI	$\text{Cs}_2[\text{Mo}(\text{NO})\text{Cl}_5]$		204

...contd.

Table I.5(contd.)

1	2	3	4	5
6. $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})_2\text{Cl}]$	$\text{Na}[\text{AlH}_2\text{-(OCH}_2\text{CH}_2\text{-OMe)}_2]$	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NO})_2\text{H}]^+$	In toluene	205
7. $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NO})_2\text{H}]$	$\text{Ph}_3\text{C}^+$ or tropylium ion	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{NO})_4\text{H}]^+$	In $\text{CH}_2\text{Cl}_2$ Reactant: Reagent, 2:1	206
8. $[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$	L or $\text{L}_2$	$[\text{Mo}(\text{NO})_2\text{L}_2\text{Cl}_2]$	L = $\text{CH}_3\text{CN}$ , $\text{PhCN}$ , $\text{PPh}_3$ or Py $\text{L}_2$ = 2,2'-Bipyridyl, 1,2-bis(diphenyl- phosphinoethane)	207
9. $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$	L	$\text{cis-}[\text{Mo}(\text{NO})_2\text{L}_4]_{x_2}$ $\xrightarrow[\text{Na}[\text{Ph}_2\text{CO}] \text{ in } \text{CH}_3\text{CN}]{\text{Na/Hg, Li/Et}_3\text{BH,}} \text{or THF}$ $[\text{Mo}(\text{NO})_2\text{L}_2]_2^{2+}$	L = $\text{CH}_3\text{CN}$ , $\text{OPh}_3$ , 2,2'-Bipyridine, X = $\text{PF}_6$ , $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ X = $\text{PF}_6$ , $\text{BF}_4$ $\text{L}_2$ = 2,2'-Bipyridine, 3,4,7,8-tetramethyl 1,10-phenanthroline	105
10. $[\text{WCl}_3(\text{PPh}_3)_2\text{NO}]$	PhSH	$[\text{PPh}_4][\text{WCl}(\text{SPh})_3(\text{NO})]$	In Methanol in presence of $\text{Et}_3\text{N}$ and $\text{PPh}_4\text{Br}$	208

Table I.5(contd.)

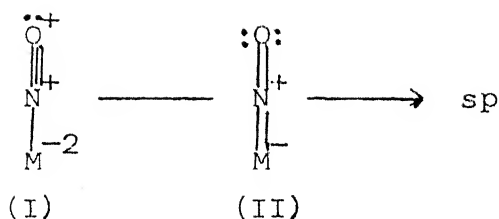
1	2	3	4	5
11. $[\text{W}(\text{CO})_2\text{Cl}(\text{NO})(\text{PPh}_3)_2]$	$\text{CH}_3\text{Li}$	$[\text{WCH}_3(\text{CO})_2(\text{NO})(\text{PPh}_3)_2]$	In THF	209
12. $[\text{W}(\text{CO})_2\text{H}(\text{NO})(\text{PPh}_3)_2]$	$\text{HX}(\text{X}=\text{Cl}, \text{Br}, \text{I},$ $\text{O}_2\text{CHO}_2\text{CCH}_3)$	$[\text{W}(\text{CO})_2\text{X}(\text{NO})(\text{PPh}_3)_2]$	$\text{CH}_2\text{Cl}_2$	210
13. $[\text{cpW}(\text{NO})_2\text{L}]\text{BF}_4 + \text{cp}_2\text{Co}$		$[\text{cpW}(\text{NO})_2\text{L}]^+ + [\text{cp}_2\text{Co}]^-$ $\text{BF}_4\text{CH}_2\text{Cl}$	$\text{L} = \text{PPh}_3,$ $\text{P}(\text{OMe})_3$	211

## I.2C Structure and bonding mode of nitric oxide in transition metal complexes

In transition metal nitrosyl complexes, nitrosyl group is generally considered to be bonded through the nitrogen atom. Although substantial evidence has accumulated for metal nitrogen coordination in metal nitrosyls, there are also a few cases where there is a possibility of bonding between metal and oxygen atom of NO [212]. However the following are three principal modes of bonding in nitrosyl complexes when metal is bonded through N or NO.

### (1) Terminal (linear M-NO) bonding

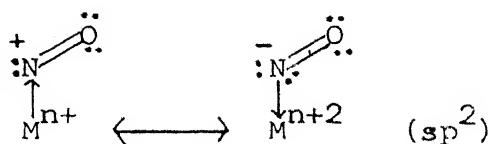
In this mode of bonding it is assumed that there is first a transfer of unpaired electron from the  $\pi$  orbital of NO to the metal atom, followed by the formation of a  $\sigma$  bond as a result of interaction of a lone pair of electrons on nitrogen atom of  $\text{NO}^+$  ion with the metal orbital. This sigma donation is reinforced by the  $\pi$  back donation from metal to  $\pi$  orbital of  $\text{NO}^+$ . In this scheme the coordination of NO to the metal thus takes place in the form of three electron donation. From the molecular orbital description it is apparent that the  $\pi$  bonding description leads to the linear mode of coordination. However the wide variation of the position of ( $\nu_{\text{NO}}$ ) in this type of coordination is a bit misleading which can be best rationalized from the valence bond picture.



In this type of bonding the nitrogen atom of nitric oxide is in  $sp$  hybridization with  $M-N-O$  bond angle remains in the region  $175-180^\circ$  and the observed bond length is found to be shorter than the normal single bond distance suggesting multiple nature of  $M-N$  bond.

## (2) Terminal bent ( $M-N-O$ ) bonding

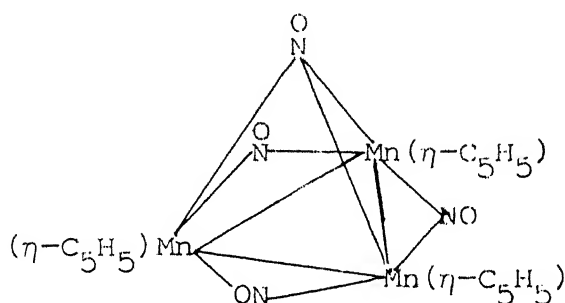
This is other extreme of bonding of  $NO$  in the metal nitrosyl complexes. Here metal nitrogen and oxygen atoms are not colinear. Here  $NO^+$  is believed to behave as a Lewis acid and accepts an electron pair from the metal (base) to  $NO^+$ . It suggests that  $NO$  can be treated formally as one electron donor and resulting charge on  $NO$  should be  $NO^-$ . In terms of valence bond representation, the bonding can be written by the following two canonical forms.



In this type of bonding the nitrogen atom of nitric oxide is in  $sp^2$  hybridisation with  $M-N-O$  bond angle in the region  $120-125^\circ$ . It has a longer  $NO$  bond length and a large trans influence.

### (3) Bridging M-N-O binding

The nitrosyl group like carbonyl group can also form bridge between two or three metal atoms, an example of the complex having bridged NO group is  $[\text{Mn}(\eta^5\text{C}_5\text{H}_5)_3(\text{NO})_4]$ .



Bridging Mode of Binding

Although some principles and generalisations have been derived from structural [100,101,104] and spectral data [213,217] of nitrosyl complexes, a complete assignment of the factors that determine one type of bonding over the other has not been fully described.

#### C.1 Infrared spectral studies

The infrared spectroscopy provides one of the most convenient methods of characterization of bonding modes of metal nitrosyls. Nitrosyl complexes have a characteristic intense absorption in the region  $1500\text{--}2000\text{ cm}^{-1}$ . The NO frequency in the linear M-NO structure generally appears at higher value than that in the bent

structure [216]. Attempts have been made to relate the positions of the absorption bands due to  $\nu_{\text{NO}}$  to the charge present on the nitrosyl group. This rule is, however misleading, since the position of  $\nu_{\text{NO}}$  depends on the coordination number, the oxidation state of the metal ion in the complex and its geometry. There is so much overlap in the  $\nu_{\text{NO}}$  frequencies of linear and bent nitrosyls in 1600–1720  $\text{cm}^{-1}$  range that a definite assignment to a particular configuration is not generally possible.

Ibers [217] after examining several hundred nitrosyl complexes, has however, proposed a set of rules relating the position of ( $\nu_{\text{NO}}$ ) and its mode of binding in the complexes. According to him the following corrections in the stretching frequencies of NO, should be made in the observed frequency of ( $\nu_{\text{NO}}$ ),

- (i) subtraction of 50, 30 and zero from the value of ( $\nu_{\text{NO}}$ ) for the first, second and third row transition metal ions, respectively.
- (ii) Addition of 100, 50 and zero in the frequency values of ( $\nu_{\text{NO}}$ ) for VIB, VIIB and VIIIB group metal ions respectively.
- (iii) Subtraction of 140 and 80 for complex ions having charge +2 and +1 respectively. Addition of 80, 140 and 200 for the complex ions having charge -1, -2 and -3 respectively.
- (iv) Addition of 20, 50, 60 and 20 for third  $\text{PR}_3$  fourth  $\text{PR}_3$ ,  $\text{C}_6\text{H}_4\text{PR}_3$  and  $\text{H}^-$  respectively.
- (v) Addition of 50 for four coordination complex.

After applying these corrections, the stretching frequencies of ( $\nu_{\text{NO}}$ ) fall at least in to two groups.

- (a) The complexes, having ( $\nu_{\text{NO}}$ ) below  $1610\text{--}1620\text{ cm}^{-1}$  will have bent nitrosyl ligand.
- (b) The complexes having ( $\nu_{\text{NO}}$ ) about  $1610\text{--}1620\text{ cm}^{-1}$  will have linear nitrosyl ligand.

Attempts have also been made to assign bent or linear M-NO structures on the basis of  $\Delta$  (the difference between  $\nu(15_{\text{NO}})$  and  $\nu(14_{\text{NO}})$ ) [219-220]. Complexes containing linear nitrosyl, have  $\Delta$  value between  $36$  and  $44\text{ cm}^{-1}$  whereas those containing bent nitrosyl, have  $\Delta$  values between  $25\text{--}28\text{ cm}^{-1}$ .

In the spectra of those nitrosyl complexes where the position of ( $\nu_{\text{NO}}$ ) occurs at  $1500\text{ cm}^{-1}$  and slightly below, nitrosyl group acts as a bridging ligand between two metal centres [221-222]. The coordinated hyponitrite,  $\text{N}_2\text{O}_2^{2-}$ , absorbs around  $1185$ ,  $1045$  and  $930\text{ cm}^{-1}$  [223-225].

#### Prediction of coordination geometries in nitrosyl complexes

Eight empirical rules have been formulated by Ibers [226] for predicting the geometry of transition metal nitrosyl complexes.

- (1) Without the assistance of special ligands, first row transition metals usually do not have enough reducing power by themselves to bend the nitrosyl ligand, second row metals often do and third row metals usually do.

- (2) The number and size of bulky ligands play an important role; they usually go in the least sterically hindered positions. With one such ligand present, it usually occupies the non axial position, with two present, both are usually trans to each other and occupy the axial sites in TBP and non axial in SP. With three present, the SP geometry is usually not found, and all three would occupy the non axial sites in TBP.
- (3) Strong  $\pi$  acceptor ligands cf. CO and NO (linear) and also  $\sigma$  donor ligands with large trans effect, such as  $H^-$  and (NO) bent, prefer not to be trans to each other in any combination if possible.
- (4) Re and probably W and Mo, which form strong metal nitrogen multiple bonds and prefer ligands which are good  $\pi$  acceptors, retard the bending of attached nitrosyl ligand.
- (5) Bidentate ligands such as tetramethylethylenediamine, 1,10-phenanthroline, 2,2'-bipyridine, O-phenylene bis(dimethyl arsine) and 1,2-bis(diphenylphosphine)ethane, usually favour TBP geometry with equatorial NO, when two such ligands are present.
- (6) Special multidentate ligands can promote one geometry over another,  $HC(CH_2PH_2)_3$  stabilized the TBP geometry.
- (7) Ligands which deactivate the metal by removing the electron density from it, thereby decreasing its reducing power, favour the TBP geometry and conversely.

- (8) If the integrity of the nitrosyl ligand is maintained, all 20-electron systems must have bent nitrosyls. Six coordinated 18-electron and 17 electron nitrosyl complexes all have linear nitrosyl ligands. Six coordinate 19 electron systems probably have partially bent NO, with M-NO angles distinctly larger than  $120^\circ$ . All 16 electron systems have linear nitrosyl ligand.

## C.2 $^{15}\text{N}$ NMR

Few reports have recently appeared [227-229] describing the attempts of correlating the positions of  $^{15}\text{N}$  NMR signals in the NMR spectrum with the geometry of M-NO group in the metal nitrosyls. The correlation is based on the premise, that there is a large difference in the nitrogen shifts in the bent compared to that shown by the linear nitrosyl ligand in solution. Although an extensive work is needed in this direction before any general rule is given to distinguish between the two types of nitrosyls, it is possible to state from the present observations [228] that  $^{15}\text{N}$  NMR of bent nitrosyls show large down field shifts (by hundreds of ppm) as compared with linear nitrosyl ligand. In the following (table I.6)  $\delta(^{15}\text{N})$  values along with  $\nu_{\text{NO}}$  values of some nitrosyl complexes studied so far are being given to illustrate the potential of the present technique.

Table I.6.  $^{15}\text{N}$  NMR and IR measurements of transition metal nitrosyl complexes

Complex	Solvent	$\delta(^{15}\text{N})$ ppm	$(\nu_{\text{NO}})$ $\text{cm}^{-1}$
<u>Linear M-N-O</u>			
<u><math>\{\text{M-NO}\}^6</math> Octahedral</u>			
$[\text{Ru}(^{15}\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$	$\text{CD}_2\text{Cl}_2$	-36.7	-
$[\text{Ru}(^{15}\text{NO})\text{Cl}_3(\text{PMePh}_2)_2]$	$\text{CD}_2\text{Cl}_2$	-30.9	1876
<u><math>\{\text{M-NO}\}^8</math> Square Planar</u>			
$\text{trans-}[\text{RhCl}(^{15}\text{NO})(\text{P-}i\text{-Pr}_3)_2]\text{ClO}_4$	$\text{CD}_2\text{Cl}_2$	24.0	1880
<u><math>\{\text{M-NO}\}^6</math> Piano Stool</u>			
$[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NO})]$	$\text{CHCl}_3$	49.0	1680
$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NO})]$	$\text{CHCl}_3$	37.6	1663
$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)(\text{NO})]$	$\text{CHCl}_3$	35.4	1607
$[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NO})]$	$\text{CHCl}_3$	16.5	1655
<u><math>\{\text{M}(\text{NO})_2\}^8</math> Dinitrosyl</u>			
$[\text{RuCl}(^{15}\text{NO})_2(\text{PPh}_3)_2](\text{BF}_4)$	$(\text{CD}_3)_2\text{CO}$	131.5	1845, 1687
<u><math>\{\text{M-NO}\}^6</math> Piano Stool</u>			
$[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{NO})_2]$	$\text{CHCl}_3$	184.6	1816, 1711
$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{NO})_2]$	$\text{CHCl}_3$	185.4	1759, 1655
$[\text{W}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{NO})_2]$	$\text{CHCl}_3$	172.9	1733, 1650

...contd.

Table I.6 (contd.)

Complex	Solvent	$\delta(^{15}\text{N})$ ppm	$(\nu_{\text{NO}})$ cm <sup>-1</sup>
<u>Bent M-N-O</u>			
<u><math>\{\text{M-NO}\}^8</math> Square Pyramidal</u>			
trans-[RuCl(CO)( <sup>15</sup> NO)(P-i-Pr <sub>3</sub> ) <sub>2</sub> ]- (ClO <sub>4</sub> )	CD <sub>2</sub> Cl <sub>2</sub>	368.2	1712
trans-[RhCl( <sup>15</sup> NO)(NO <sub>2</sub> )(Pcy <sub>3</sub> ) <sub>2</sub> ]	CD <sub>2</sub> Cl <sub>2</sub>	466.1	1684, 1654
trans-[RhCl( <sup>15</sup> NO)(NO <sub>2</sub> )(P-i-Pr <sub>3</sub> ) <sub>2</sub> ]	CD <sub>2</sub> Cl <sub>2</sub>	467.6	1684, 1657
trans-[RhCl( <sup>15</sup> NO)(NO <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	CD <sub>2</sub> Cl <sub>2</sub>	481.5	1657, 1629

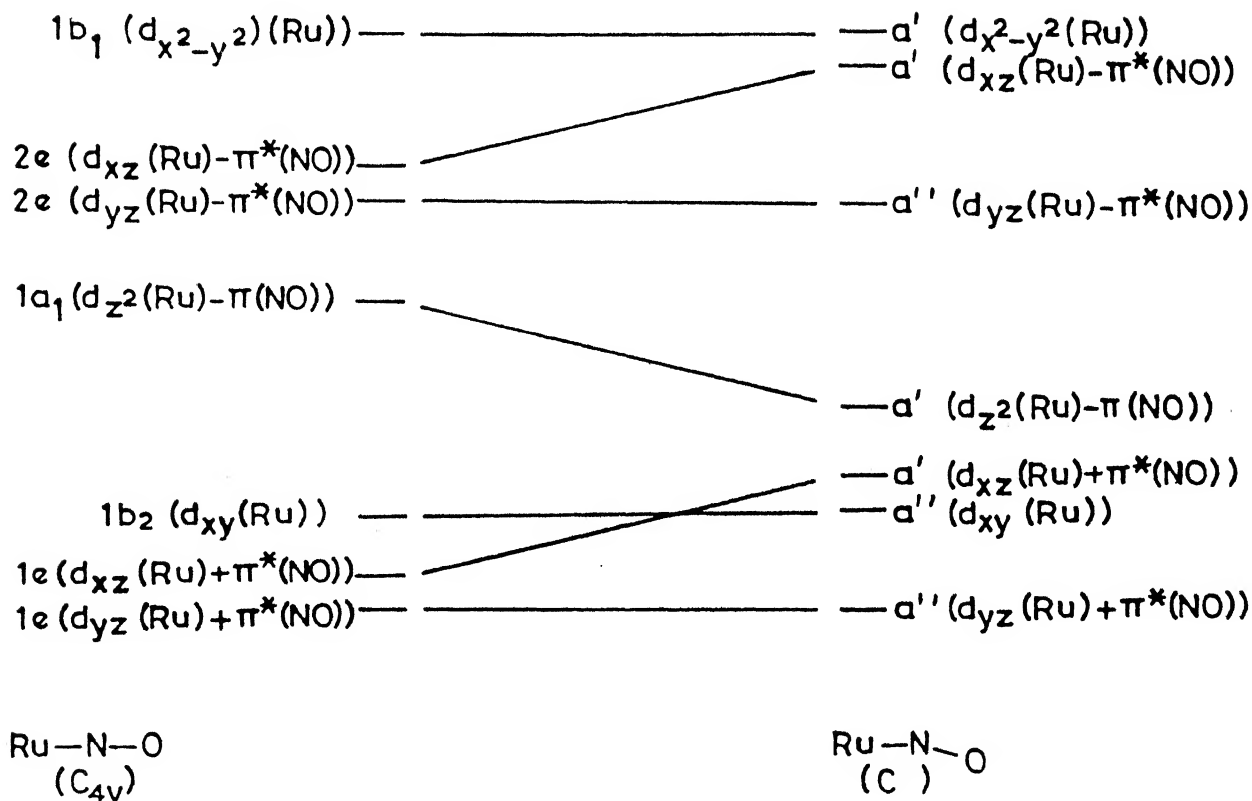
#### C.4 ESCA studies

Recently ESCA [205,230-232] has provided a complementary data to that of infrared to distinguish between the bent and linear nitrosyls. Fuller, et al. [216] have attempted to establish a correlation between nitrosyl bonding modes and the difference of the bonding energies of N(1s) and O(1s) of nitrosyl group. It is tentatively found that the relative shifts of the binding energies of O(1s) and N(1s) electrons in the range of  $132 \pm 1$  eV, suggests the presence of a linear nitrosyl group and that, in the range of  $128 \pm 2$  eV, bent nitrosyls. Because of difficulties in the sample preparation, relatively few complexes have so far been studied (which makes a boundary limit rather wide). It is unlikely that

this interesting technique will be able to supplement the simple infrared method for deciding between the linear and bent nitrosyls.

#### C.4 Molecular Orbital Theory of bonding in Metal Nitrosyls

The nature of bonding in the transition metal nitrosyls have also been described in the terms of molecular orbital theory by a number of worker [66,233-235]. From the foregoing discussions it is clear that vibrational spectral studies of metal nitrosyls provide considerable power in predicting geometries and possible reactivity pattern of nitrosyls. Although molecular orbital approach is presently lacking in the simple gross predictive power, it has however, rationalized a number of seeming contradictions, and provided a very unified view of nitrosyl chemistry. In this approach the description of six coordinate linear  $\{\text{RuNO}\}^6$  (according to Enemark and Feltham's [66] suggested notations, metal nitrosyls can be designated as  $\{\text{MNO}\}^n$  where  $n$  is the number of d-electrons of the metal  $M$  plus the number of electrons in the  $\pi^*$  orbital of NO) implies that the  $dxz(\text{Ru}) + \pi^*(\text{NO})$ ,  $dyz(\text{Ru}) + \pi^*(\text{NO})$  and  $dxy(\text{Ru})$  orbitals are filled, with the antibonding  $dz^2(\text{Ru})-n(\text{NO})$ ,  $dyz(\text{Ru})-\pi^*(\text{NO})$ ,  $dxz(\text{Ru})-\pi^*(\text{NO})$  and  $dx^2-y^2(\text{Ru})$  orbitals are empty (fig.1) [66,233-235]. This approach stresses the extremely important role of  $\pi^*(\text{NO})$  orbital in transferring charge from Ru to NO, and thus its role in metal ligand bond. The  $\pi$  orbitals on NO are so polarized such that there is an increased  $e^-$  density at O, rather than on N atom [89]. As with the simple  $\text{Ru(II)}-\text{NO}^+$  approach, potential electrophillic behaviour at N and nucleophilic behaviour at O are anticipated.



Energy level diagram for linear and bent {RuNo} complexes

FIG. 1.1

Table I.7. Physical parameters of NO.

Parameters	NO
Bond length (pm)	115.1
IR frequency ( $\text{cm}^{-1}$ )	1876
Dipolemoment (D)	$0.158 \pm 0.005$
Rotational constant $B_0$ ( $\text{cm}^{-1}$ )	1.6957
Fine structure constant A ( $\text{cm}^{-1}$ )	$123.160 \pm 0.02$
Hyperfine constant (MHz)	$75.81 \pm 0.24$
Quardupole coupling constant Q	$1.8 \pm 0.3$
Ionization potential (eV) (NX — NX <sup>+</sup> + e <sup>-</sup> )	9.8

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## CHAPTER TWO

### N-ACETYL-DL-PENICILLAMINE THIONITRITE A POTENTIAL NITROSYLATING AGENT

N-Acetyl-DL-penicillamine thionitrite (hereafter referred to as PT), because of its being the most stable, easily synthesizable, and unlike other nitrosylating agents  $\text{NO}$ ,  $\text{NOX}(\text{X}=\text{Cl}^-, \text{Br}^-, \text{Br}_3^-)$  and nitrosamines not having any harmful effects, will possibly make the nitrosylation study an interesting one. Besides, it seems possible to synthesize nitrosyls at elevated temperatures by combining its thermal instability only at higher temperatures with the trapping of  $\text{NO}$  radical by the metal ions. This behaviour appears to be similar, if not better, to that of well established nitrosylating agent, N-methyl-N-nitrosotoluene-p-sulphonamide, (MNTS). Hence nitrosylation reactions taking place at higher temperatures were especially attempted to make a direct comparison to those by MNTS. Furthermore, wide spread interest in PT for the syntheses of antibiotics and of metal chelates for the biomedical applications

further enhanced our interest. The present chapter reports the result of such a study and the use of PT as a source for a single stage metal nitrosylation reactions of Ru, Rh, Ir, Co and Mo.

## II.A Experimental

All the experiments were carried out under nitrogen. Solvents and reagents were purified by standard methods and degassed. N-acetyl-DL-penicillaminethionitrite (PT) and the starting complexes of Ru, Rh and Ir were prepared and purified by the literature procedures [1-19].

### II.B.1 Reactions of penicillamine thionitrite with $MCl_3 \cdot xH_2O$ (M = Ru, Rh, Ir), $CoCl_2 \cdot 6H_2O$ , $Mo(CO)_6$ in presence of $PPh_3$ , $AsPh_3$ , $SbPh_3$ and ethylenediamine

#### (I) Reaction of PT with $RuCl_3 \cdot xH_2O$ in presence of triphenylphosphine

Solutions of  $RuCl_3 \cdot xH_2O$  (0.5 mmol) in ethanol (10 ml) and PT (1.0 mmol) in ethanol (10 ml) were added to a vigorously stirred boiling solution of triphenylphosphine (2 mmol) in ethanol (20 ml). The resulting mixture was heated under reflux for about half an hour whereupon orange yellow crystals were separated. These were filtered, washed with ethanol, water, ethanol and finally with diethyl ether and dried in vacuo. The complex after recrystallization from  $CH_2Cl_2/MeOH$  melted at  $228^\circ C$ . It was analysed for

$[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ . The same product was obtained when the reaction was carried out in presence of  $\text{HgCl}_2$  or dry  $\text{HCl}$  gas.

(II) Reaction of PT with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylarsine

The same method as described in [II.B.1(I)] was followed to carry out the reaction except that triphenylarsine was used in place of triphenylphosphine. The compound obtained as reaction product was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , washed with methanol and diethyl ether and dried in vacuo (m.p.  $> 290^\circ\text{C}$ ). It was analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$ .

(III) Reaction of PT with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylstibine

The same procedure as described in [II.B.1(I)] was adopted to carry out the reaction except that triphenylstibine was used in place of triphenylphosphine. The orange red compound obtained as reaction product was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , washed with methanol, ether and dried in vacuo (m.p.  $220^\circ\text{C}$ ). It was analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$ .

(IV) Reaction of PT with  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylphosphine

Mixed solutions of  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  (0.5 mmol) in ethanol (10 ml) and PT (1.0 mmol) in ethanol (10 ml) was added to a vigorously stirred boiling solution of triphenylphosphine (2 mmol) in (20 ml)

of ethanol. The resulting reaction mixture was heated under reflux for about half an hour whereby orange yellow shiny crystals were separated. These were centrifuged, washed with ethanol, water, ethanol and ether and dried in vacuo. The complex after recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , melted at  $222^\circ\text{C}$  and analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ .

The same product was obtained when the reaction was carried out in presence of  $\text{HCl}$  gas or  $\text{HgCl}_2$ .

(V) Reaction of PT with  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylarsine

The same procedure as described in [II.B.1(IV)] was adopted to carry out the reaction except that triphenylarsine was added in place of triphenylphosphine. The crude crystals obtained after the reaction was over, were recrystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , washed with methanol, ether, (m.p.  $245^\circ\text{C}$ ). It was analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2-(\text{AsPh}_3)_2]$ .

(VI) Reaction of PT with  $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylphosphine

Solutions of  $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$  (0.5 mmol) in 2-methoxyethanol (10 ml) and PT (1.0 mmol) in 2-methoxyethanol (10 ml) were added successively to a well stirred solution of triphenylphosphine (2 mmol) in (20 ml) 2-methoxyethanol. The resulting reaction mixture was heated under reflux for about half an hour whereupon an orange yellow crystalline

compound separated out. It was separated by centrifugation washed with ethanol, water, ethanol and ether and dried in vacuo. It melted at  $247^{\circ}\text{C}$  and was analysed for  $[\text{Ir}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ .

(VII) Reaction of PT with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in presence of ethylenediamine

A methanolic solution (40 ml) of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (3 mmol) and PT (6 mmol) in methanol (15 ml) were mixed successively with a methanolic solution (10 ml) of ethylenediamine (12 mmol). The resulting mixture on heating under reflux for about half an hour afforded an orange microcrystalline compound, which, on cooling to room temperature, was separated by filtration. It was washed with methanol, ether and dried in vacuo. The compound was analysed for  $[\text{Co}(\text{en})_2\text{NOCl}]\text{Cl}$ .

(VIII) Reaction of PT with  $\text{Mo}(\text{CO})_6$  in presence of triphenylphosphine and dry chlorine gas

25 ml of a warm benzene solution containing  $\text{Mo}(\text{CO})_6$  (0.26 gms) and PT (2 mmol) was added to a well stirred boiling benzene solution (25 ml) of triphenylphosphine (5 mmol). The resulting mixture was heated under reflux for about half an hour while passing a slow stream of dry chlorine gas through the solution. The refluxing was further continued for another half an hour whereby a pale green coloured compound separated. It was separated by filtration.

The complex was extracted with dichloromethane. On adding light petroleum ether to the  $\text{CH}_2\text{Cl}_2$  extract, a yellow green compound was separated, which was filtered, washed with petroleum ether and dried in vacuo (m.p.  $165^\circ\text{C}$ ). It was analysed for  $[\{\text{MoCl}_2(\text{PPh}_3)_2\}_2]^{2-} \text{N}_2\text{O}_2] \text{Cl}_2$ .

## II.B.2 Reactions of PT with the complexes of ruthenium and rhodium

### (I) Reaction of PT with $[\text{RuCl}_2(\text{PPh}_3)_3]$

A solution of PT (1.5 mmol) in warm ethanol (5 ml) was added to a (10 ml) hot dichloromethane solution of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  (0.2 mmol). The reaction mixture was refluxed with vigorous stirring for about half an hour whereby a brown precipitate was separated. It was separated by filtration after cooling it to room temperature. It was washed with ethanol, water, ethanol and ether and dried in vacuo. The shiny crystals of the product melted at  $230^\circ\text{C}$ . The analytical data, m.p., mixed m.p., i.r. spectrum and other physical data match with those of authentic sample of  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ .

The same compound was obtained if the reaction was carried out in presence of dry HCl gas or  $\text{HgCl}_2$ .

### (II) Reaction of PT with $[\text{RuCl}_2(\text{PPh}_3)_4]$

The reaction was carried out by the same procedure as described in [II.B.2(I)] except that  $[\text{RuCl}_2(\text{PPh}_3)_4]$  was used in place of

$[\text{RuCl}_2(\text{PPh}_3)_3]$ . The reaction product was identified as  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ .

(III) Reaction of PT with  $[\text{RuH}_2(\text{PPh}_3)_3]$  in presence of dry HCl gas

The reaction was performed by the method as described in II.B.2(I) except that  $[\text{RuH}_2(\text{PPh}_3)_3]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  while passing dry HCl gas intermittantly through the reaction mixture. Shiny crystals of  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$  were obtained as the reaction product.

(IV) Reaction of PT with  $[\text{Ru}(\text{CO})\text{Cl}_2(\text{PPh}_3)_3]$

The reaction was carried out by the same procedure as described in [II.B.2(I)] except that  $[\text{Ru}(\text{CO})\text{Cl}_2(\text{PPh}_3)_3]$  was used in the place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . It yielded  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$  as the final product.

(V) Reaction of PT with  $[\text{RuCl}_2(\text{PPh}_3)_2 \cdot \text{MeOH}]$

The procedure adopted to carry out the reaction was the same as described in [II.B.2(I)] except that  $[\text{RuCl}_2(\text{PPh}_3)_2 \cdot \text{MeOH}]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The reaction product was found to be  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ .

(VI) Reaction of PT with  $[\text{Ru}(\text{cp})\text{Cl}(\text{PPh}_3)_2]$  in presence of HCl gas

A warm solution of PT (1.5 mmol) in ethanol (5 ml) was added to a solution of  $[\text{Ru}(\text{cp})\text{Cl}(\text{PPh}_3)_2]$  (0.2 mmol) in a mixture of dichloromethane and ethanol (20 ml,  $\text{EtOH}:\text{CH}_2\text{Cl}_2$ , 1:2). The resulting solution was refluxed for about half an hour. During refluxing, HCl gas was allowed to pass intermittently. A deep red coloured solution was obtained, which on cooling to room temperature, yielded yellow orange crystals. They were separated by centrifugation, washed with ethanol, ether and dried in vacuo. The crystals were analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ .

(VII) Reaction of PT with  $[\text{RuCl}_3(\text{AsPh}_3)_3]$

The reaction was carried out by using the same methodology as described in [II.B.2(I)] except that  $[\text{RuCl}_3(\text{AsPh}_3)_3]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The reaction product analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$ .

(VIII) Reaction of PT with  $[\text{RuCl}_3(\text{AsPh}_3)_2\cdot\text{MeOH}]$

The reaction was carried out by following the same procedure as described in [II.B.2(I)] except that  $[\text{RuCl}_3(\text{AsPh}_3)_3]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The crystals obtained were analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$ .

(IX) Reaction of PT with  $[\text{Ru}(\text{CO})\text{Cl}_2(\text{AsPh}_3)_3]$ 

The reaction was carried out by the same procedure as described in [II.B.2(1)] except that  $[\text{Ru}(\text{CO})\text{Cl}_2(\text{AsPh}_3)_2]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The reaction product was identified as  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$ .

(X) Reaction of PT with  $[\text{RuH}(\text{CO})\text{Cl}(\text{PPh}_3)_3]$ 

The same procedure as described in [II.B.2(I)] was adopted except that  $[\text{RuH}(\text{CO})(\text{PPh}_3)_3]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The reaction yielded a shiny yellow microcrystalline compound, whose analytical and spectral data indicated it to be a mixture of two compounds. Since one of the components was relatively more soluble in benzene, both the components were separated by fractional crystallization using benzene/dichloromethane. The benzene fraction was crystallized using light petroleum ether while the other by  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ . The benzene soluble fraction melted at  $228^\circ\text{C}$  and analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$  and the fraction which was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  was identified as  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2]$  (m.p.  $233^\circ\text{C}$ ).

(XI) Reaction of PT with  $[\text{Ru}\{(\text{OPh})_3\text{P}\}_4\text{Cl}_2]$ 

The reaction was carried out by the same procedure as described in [II.B.2(I)] except that  $[\text{Ru}\{(\text{OPh})_3\text{P}\}_4\text{Cl}_2]$  was used in place of

$[\text{RuCl}_2(\text{PPh}_3)_3]$ . The final product of the reaction was identified as  $[\text{Ru}(\text{NO})\text{Cl}_3\{(\text{OPh})_3\text{P}\}_2]$ .

(XII) Reaction of PT with  $[\text{RhCl}(\text{PPh}_3)_3]$

A solution of PT (4 mmol) in ethanol (10 ml) was added to a red coloured dichloromethane solution (10 ml) of  $[\text{RhCl}(\text{PPh}_3)_3]$  (0.2 mmol). The resulting solution was heated to reflux for about half an hour whereupon a deep red coloured solution was obtained. After cooling it to room temperature shiny orange crystals separated out, which were separated by filtration, washed with ethanol, water, ethanol, ether and dried in vacuo. The crystals which melted at  $224^\circ\text{C}$  were analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ .

(XIII) Reaction of PT with  $[\text{RhCl}(\text{PPh}_3)_2]_2$

The reaction was carried by the same procedure as described in [II.B.2(XII)] except that  $[\text{RhCl}(\text{PPh}_3)_2]_2$  was used in place of  $[\text{RhCl}(\text{PPh}_3)_3]$ . The final product of the reaction was analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ .

(XIV) Reaction of PT with  $[\text{RhH}(\text{PPh}_3)_3]$

The reaction was performed by the method as described in [II.B.2(XII)] except that  $[\text{RhH}(\text{PPh}_3)_3]$  was used in place of  $[\text{RhCl}(\text{PPh}_3)_3]$ . Shiny crystals of  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$  were obtained as the reaction product.

(XV) Reaction of PT with  $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$  in presence of HCl

The reaction was performed by the method as described in [II.B.2(XII)] except that  $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$  was used in place of  $[\text{RhCl}(\text{PPh}_3)_3]$  and during refluxing a slow stream of HCl gas was allowed to pass through the reaction mixture. The final product obtained was identified as  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ .

(XVI) Reaction of PT with  $[\text{Rh}(\text{CO})\text{Cl}(\text{AsPh}_3)_2]$  in presence of HCl

The reaction was carried out by the same procedure as described in [II.B.2(XII)] except that  $[\text{Rh}(\text{CO})\text{Cl}(\text{AsPh}_3)_2]$  was used in place of  $[\text{RhCl}(\text{PPh}_3)_3]$  and during refluxing a stream of dry HCl gas was allowed to pass intermittantly. The product obtained was analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{AsPh}_3)_2]$ .

(XVII) Reaction of PT with  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylphosphine and  $\text{NaBH}_4$

Hydrated  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  (0.5 mmol) in ethanol (10 ml), PT (1.0 mmol) in ethanol (10 ml), and sodium borohydride (0.10 g) in ethanol (10 ml) were added rapidly in succession to a well stirred solution of triphenylphosphine (2.0 mmol) in ethanol (40 ml). The mixture was heated under reflux for about half an hour, cooled to room temperature. The precipitate was separated by filtration, washed successively with ethanol, water, ethanol and ether and dried in

vacuo to give the product as orange red microcrystals. These were analysed for  $[\text{Rh}(\text{NO})(\text{PPh}_3)_3]$ .

(XVIII) Reaction of PT with  $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$  in presence of HCl gas

A solution of PT (2 mmol) in ethanol (10 ml) was added to a yellow suspension of  $[\text{Rh}(\text{H})\text{CO}(\text{PPh}_3)_3]$  (0.2 mmol) in ethanol (20 ml). The reaction mixture was refluxed for about half an hour. During refluxing dry HCl gas was allowed to pass intermittantly through the solution. It resulted in the formation of an orange red coloured solid which deposited in the bottom of the reaction flask. It was separated by filtration, washed repeatedly with alcohol, ether and dried in vacuo. It was analysed for  $[\text{RhCO}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$  (m.p.  $189^\circ\text{C}$ ).

(XIX) Reaction of PT with  $[\text{RhCl}(\text{AsPh}_3)_3]$

The same method as described in [II.B.2(XII)] was adopted to carry out the reaction except that  $\text{RhCl}(\text{AsPh}_3)_3$  was used in place of  $[\text{RhCl}(\text{PPh}_3)_3]$ . The compound obtained as reaction product was analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{AsPh}_3)_2]$ .

(XX) Reaction of PT with  $[\text{RhH}\{(\text{OPh})_3\text{P}\}_4]$  in presence of HCl gas

The same procedure as described in [II.B.2(XII)] was followed to carry out the reaction except that  $[\text{RhH}\{(\text{OPh})_3\text{P}\}_4]$  was used in

place of  $[\text{RhCl}(\text{PPh}_3)_3]$ . The orange compound obtained as reaction product was recrystallised from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , washed with methanol, ether and dried in vacuo. It was analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2\{(\text{OPh})_3\text{P}\}_2]$ .

## II.C Analyses and Physicochemical measurements

Carbon, hydrogen and nitrogen in the complexes were analysed by the microanalytical laboratory of the Indian Institute of Technology, Kanpur, India. Halide contents in the complexes were determined gravimetrically as  $\text{AgX}$  by the method described elsewhere [20].

Infrared spectra of the complexes were recorded either on a Perkin-Elmer model-580 diffraction grating spectrophotometer in the range  $4000\text{--}200\text{ cm}^{-1}$  or with a Shimadzu IR-420 infrared spectrophotometer in  $4000\text{--}400\text{ cm}^{-1}$  range. Samples were prepared as KBr pellets. Some of the representative spectra are given towards the end of the chapter.

Magnetic measurements were made on a Gouy Balance at room temperature. Mercury tetrathiocyanatocobaltate(II) was used as calibrant.

Melting points of the complexes were recorded on a Fisher-johns melting point apparatus in air and are uncorrected.

## II.D Results and Discussion

The homolytic thermal cleavage of S-N bond in PT resulted in the formation of metal nitrosyls. The products formed and conditions used in carrying out the reactions are given in Table II.1. Since the nitrosyls formed during the reactions are generally the literature known ones, they have been identified by their analytical, spectral (ir, uv visible) and the magnetic data. In cases where complexes melt, their mps, mixed mps were also compared with the authentic samples.

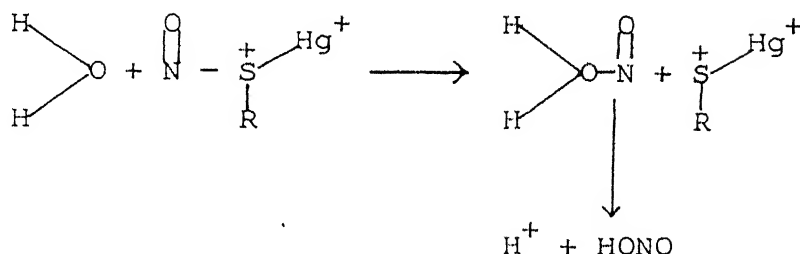
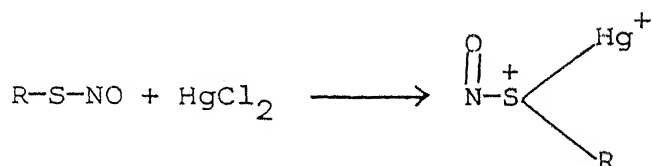
Table 1 indicates that in a couple of reactions the nitrosyls obtained were different from the expected ones. Thus the reaction of  $[\text{RuH}(\text{CO})\text{Cl}(\text{PPh}_3)_3]$  with PT did not yield the expected nitrosyl  $[\text{Ru}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]$  [21], but it formed a mixture of two complexes. Its ir spectrum exhibited a very strong band at  $1875\text{ cm}^{-1}$  and two intense bands at  $2065$  and  $1990\text{ cm}^{-1}$  corresponding to  $\nu_{\text{NO}}$  and  $\nu_{\text{CO}}$  respectively. On purification by fractional crystallization, two complexes were separated which were identified as  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$  and  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2]$ . No difference in the nature of the complex was obtained if the same reaction was carried out in presence of  $\text{HgCl}_2$  or dry  $\text{HCl}$  gas.

Reaction of  $\text{Mo}(\text{CO})_6$  with PT in presence of triphenylphosphine and dry chlorine gas yielded a compound having an empirical formula  $[\{\text{MoCl}_2(\text{PPh}_3)_2\}_2\text{N}_2\text{O}_2]\text{Cl}_2$ , whose ir spectrum exhibited strong bands at  $1145$ ,  $1034$  and  $980\text{ cm}^{-1}$ . These bands have been assigned to a

bridging  $\text{N}_2\text{O}_2^{2-}$  group coordinated through oxygen atoms. The reaction could not yield the dinitrosyl complex as expected [22,23].

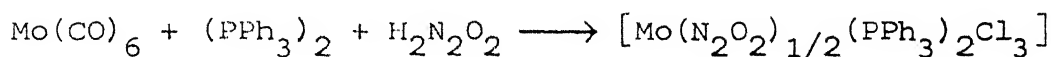
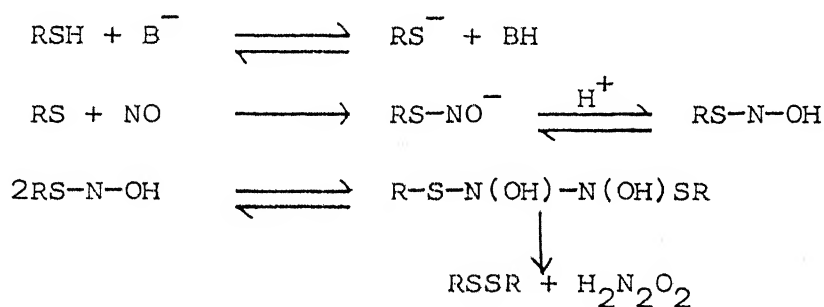
Nitrosyl complexes by the reaction of PT with platinum or palladium salts in presence of triphenylphosphine or triphenylarsine were also not obtained. This observation possibly reflects the tendency of these metals to form zero oxidation state complexes in preference to nitrosyls.

Denitrosation of PT in presence of an acid goes through the intermediacy of  $\text{HNO}_2$  ( $\text{RS-NO} + \text{H}_2\text{O} \rightleftharpoons \text{RSH} + \text{HNO}_2$ ) [24]. This is a reversible reaction with equilibrium lying well over to the side of thionitrite and thus slowing down the denitrosation rate. However if a nitrous acid trap is also included to prevent the reverse reaction (nitrosation), the rate of denitrosation reaction may be increased. Traps like  $\text{NaN}_3$ , ascorbic acid, aniline derivatives, urea, etc. have been used before [25]. Since the results of the present work suggest the successful application of PT as a nitrosylating agent for the metal ions or their complexes, it appears that the latter acted as scavengers for  $\text{HNO}_2$  leading to the nitrosylation of metal ions. However it has been found that in some cases the presence of mercuric chloride, mercuric acetate or silvernitrate affected the rates of reactions to a very large extent [26]. The increased rate could be due to the following possible mechanism.



$\text{HNO}_2$  thus formed may nitrosylate the metal ions or their complexes.

The reaction of  $\text{Mo(CO)}_6$  with PT yielded a hyponitrite complex rather than a dinitrosyl one. Interestingly it is known that in presence of a base denitrosation of nitrosothiols yield  $\text{H}_2\text{N}_2\text{O}_2$  [27]. We, therefore, propose the following tentative mechanism to be operative in the case of molybdenum with triphenylphosphine acting as a probable base.



In the reaction chlorine gas may be serving dual purpose (1) oxidation of molybdenum to higher oxidation state and (2) a source of chloride ions.

Although the work in this direction is in progress, the results of the present work indicate that the PT, similar to MNTS, may be used for the synthesis of a large number of transition metal nitrosyls at higher temperatures under simple reaction conditions.

TABLE-1

Reactions carried out and their conditions, products, colour melting point and position of  $\nu_{\text{NO}}$ 

Sl. No.	Reactants, mole ratio	Solvent	Reaction conditions	Specific reaction conditions	Reaction products (colour, m.p. °C)	$\nu_{\text{NO}}$ ( $\text{cm}^{-1}$ )
1	2	3	4	5	6	7
1.	$\text{RuCl}_3 \cdot x\text{H}_2\text{O} + \text{PPh}_3 + \text{PT}$ (0.5 mmol) (2 mmol) (1 mmol)	Ethanol	The reaction mixture was refluxed for 0.5 hour with vigorous stirring under nitrogen atmosphere	-	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ (0, 228-230°C)	1875
2.	$\text{RuCl}_3 \cdot x\text{H}_2\text{O} + \text{AsPh}_3 + \text{PT}$ (0.5 mmol) (2 mmol) (1 mmol)	- do -	- do -	-	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$ (0, did not melt)	1860
3.	$\text{RuCl}_3 \cdot x\text{H}_2\text{O} + \text{SbPh}_3 + \text{PT}$ (0.5 mmol) (2 mmol) (1 mmol)	- do -	- do -	-	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$ (OR, 220°C)	1840
4.	$[\text{RuCl}_2(\text{PPh}_3)_3] + \text{PT}$ (.2 mmol) (1.5 mmol)	Ethanol/ dichloro methane (1:1)	Reaction mixture was refluxed for 2.5 hours with vigorous stirring	-	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ (0, 228-230°C)	1875
5.	$[\text{RuCl}_2(\text{PPh}_3)_4] + \text{PT}$ (0.2 mmol) (1.5 mmol)	- do -	- do -	-	- do -	-do-
6.	$[\text{RuH}_2(\text{PPh}_3)_3] + \text{PT}$ (.2 mmol) (1.5 mmol)	- do -	- do -	dry HCl gas was passed through the reaction mixture	- do -	-do-
7.	$[\text{Ru}(\text{CO})\text{Cl}_2(\text{PPh}_3)_3] + \text{PT}$ (.2 mmol) (1.5 mmol)	- do -	- do -	-	- do -	-do-
8.	$[\text{RuCl}_3(\text{PPh}_3)_2 \cdot \text{MeOH}] + \text{PT}$ (.2 mmol) (1.5 mmol)	- do -	- do -	-	- do -	-do-

...contd.

TABLE-1 (contd.)

1	2	3	4	5	6	7
9.	$[\text{Ru}(\text{Cp})\text{Cl}(\text{PPh}_3)_2]^+ \text{PT}$ (.2 mmol)	- do -	- do -	-	- do -	-do-
10.	$[\text{RuCl}_3(\text{AsPh}_3)_3] + \text{PT}$ (.2 mmol)	- do -	- do -	-	$[\text{RuCl}_3(\text{NO})(\text{AsPh}_3)_2]$ (0, did not melt)	1860
11.	$[\text{RuCl}_3(\text{AsPh}_3)_2\text{MeOH}]^+ \text{PT}$ (.2 mmol)	- do -	- do -	-	- do -	-do-
12.	$[\text{Ru}(\text{Cp})\text{Cl}(\text{AsPh}_3)_2] + \text{PT}$ (.2 mmol)	- do -	- do -	-	- do -	-do-
13.	$[\text{Ru}(\text{CO})\text{Cl}_2(\text{AsPh}_3)_3]^+ \text{PT}$ (.2 mmol)	- do -	- do -	-	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$ (0, did not melt)	1860
14.	$[\text{RuH}(\text{CO})\text{Cl}(\text{PPh}_3)_3] + \text{PT}$ (0.7 gm)	Ethanol	- do -	-	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ (0, 228°C)	1575
15.	$[\text{Ru}(\text{OPh})_3\text{P}(\text{Cl}_2)] + \text{PT}$ (.2 mmol)	$\text{EtOH}/\text{CH}_2\text{Cl}_2$	- do -	-	$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2]$ (0, 233°C)	-
16.	$\text{RhCl}_3 \cdot x\text{H}_2\text{O} + \text{PPh}_3 + \text{PT}$ (.5 mmol) (2 mmol) (1 mmol)	Ethanol	refluxed for .5 hours with vig- orous stirring under nitrogen atmosphere	-	$[\text{Ru}(\text{NO})\text{Cl}_3\{\text{P}(\text{CPh})_3\}_2]$ (Y, 245°C)	1900
17.	$\text{RhCl}_3 \cdot x\text{H}_2\text{O} + \text{AsPh}_3 + \text{PT}$ (.5 mmol) (2 mmol) (1 mmol)	- do -	- do -	-	$[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ (0, 222°C)	1630
					$[\text{Rh}(\text{NO})\text{Cl}_2(\text{AsPh}_3)_2]$ (0, 245°C)	1625

...contd.

TABLE-1 (contd.)

1	2	3	4	5	6	7.
18.	$[\text{RuCl}(\text{PPh}_3)_3] + \text{PT}$ (.2 mmol) (4 mmol)	$\text{EtOH}/\text{CH}_2\text{Cl}_2$	refluxed for 2.5 hours	-	$[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ (0, 222°C)	1630
19.	$[\text{RhCl}(\text{PPh}_3)_2]_2 + \text{PT}$ (.2 mmol) (4 mmol)	- do -	- do -	-	- do -	-do-
20.	$[\text{RhH}(\text{PPh}_3)_3] + \text{PT}$ (.2 mmol) (2 mmol)	- do -	- do -	-	- do -	-do-
21.	$[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2] + \text{PT}$ (.2 mmol) (2 mmol)	- do -	- do -	HCl gas was passed	- do -	-do-
22.	$[\text{Rh}(\text{CO})\text{Cl}(\text{AsPh}_3)_2] + \text{PT}$ (.2 mmol) (2 mmol)	- do -	- do -	-	$[\text{RhCl}_2(\text{NO})(\text{AsPh}_3)_2]$	1625
23.	$\text{RhCl}_3 \cdot x\text{H}_2\text{O} + \text{PPh}_3 + \text{PT}$ (.5 mmol) (2 mmol) (1 mmol) + $\text{NaBH}_4$ (1 mmol)	$\text{EtOH}$	refluxed for 1.5 hours	-	$[\text{Rh}(\text{NO})(\text{PPh}_3)_3]$	1630
24.	$[\text{RhH}(\text{CO})(\text{PPh}_3)_3] + \text{PT}$ (.2 mmol) (2 mmol)	$\text{EtOH}/\text{CH}_2\text{Cl}_2$	2.5 hours	HCl gas was passed	$[\text{Rh}(\text{NO})(\text{CO})\text{Cl}_2(\text{PPh}_3)_2]$ (0, 189°C)	1630
25.	$[\text{RhCl}(\text{AsPh}_3)_3] + \text{PT}$ (.2 mmol) (4 mmol)	- do -	- do -	-	$[\text{Rh}(\text{NO})\text{Cl}_2(\text{AsPh}_3)_2]$ (0, 245°C)	1625
26.	$[\text{RhH}(\text{OPh}_3)_3] + \text{PT}$	- do -	- do -	HCl gas was passed	$[[\text{RhCl}_2(\text{NO})\{\text{P}(\text{OPh}_3)_2]$	1635

...contd.

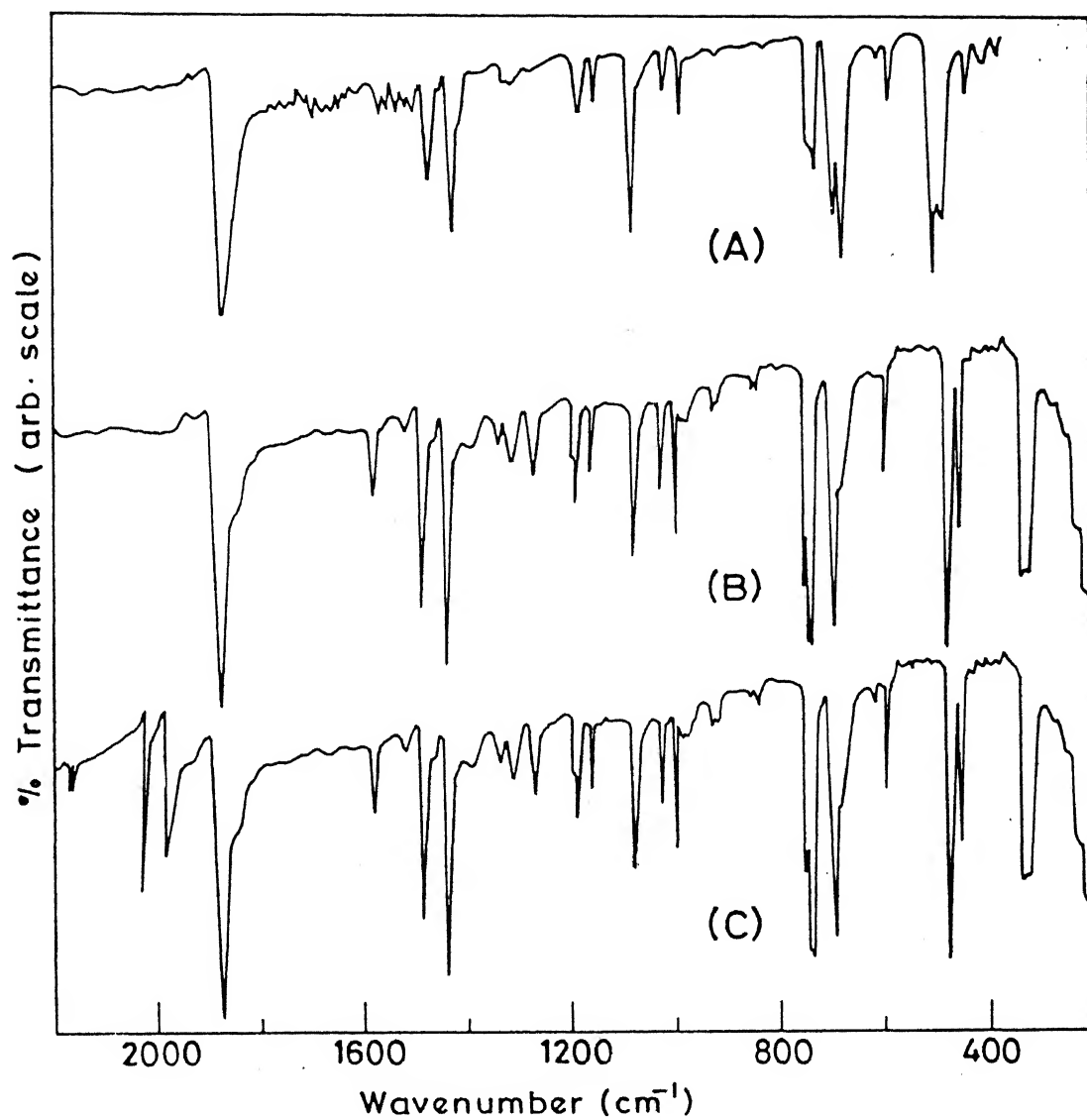
TABLE-1 (contd.)

1	2	3	4	5	6	7
27.	$\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ + $\text{PPh}_3$ + Pt (.5 mmol) (2 mmol) (2 mmol)	2-Methoxy ethanol	refluxed for .5 hour	-	$[\text{Ir}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ (OY, 247°C)	1150
28.	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ + en + Pt (3 mmol) (12 mmol) (6 mmol)	Methanol	- do -	-	$[\text{Co}(\text{en})_2\text{Cl}(\text{NO})\text{Cl}]$ (O, -)	1630
29.	$\text{Mo}(\text{CO})_6$ + $\text{PPh}_3$ + Pt (1 mmol) (5 mmol) (2 mmol)	Benzene	- do -	$\text{Cl}_2$ gas was passed	$[\text{MoCl}_2(\text{PPh}_3)_2\text{H}_2\text{O}_2\text{Cl}_2]$ (YB, 165°C)	1145, 1034, 980

O, Orange; Y, Yellow; YB, Yellow Orange; OR, Orange Red; YB, Yellow Green.

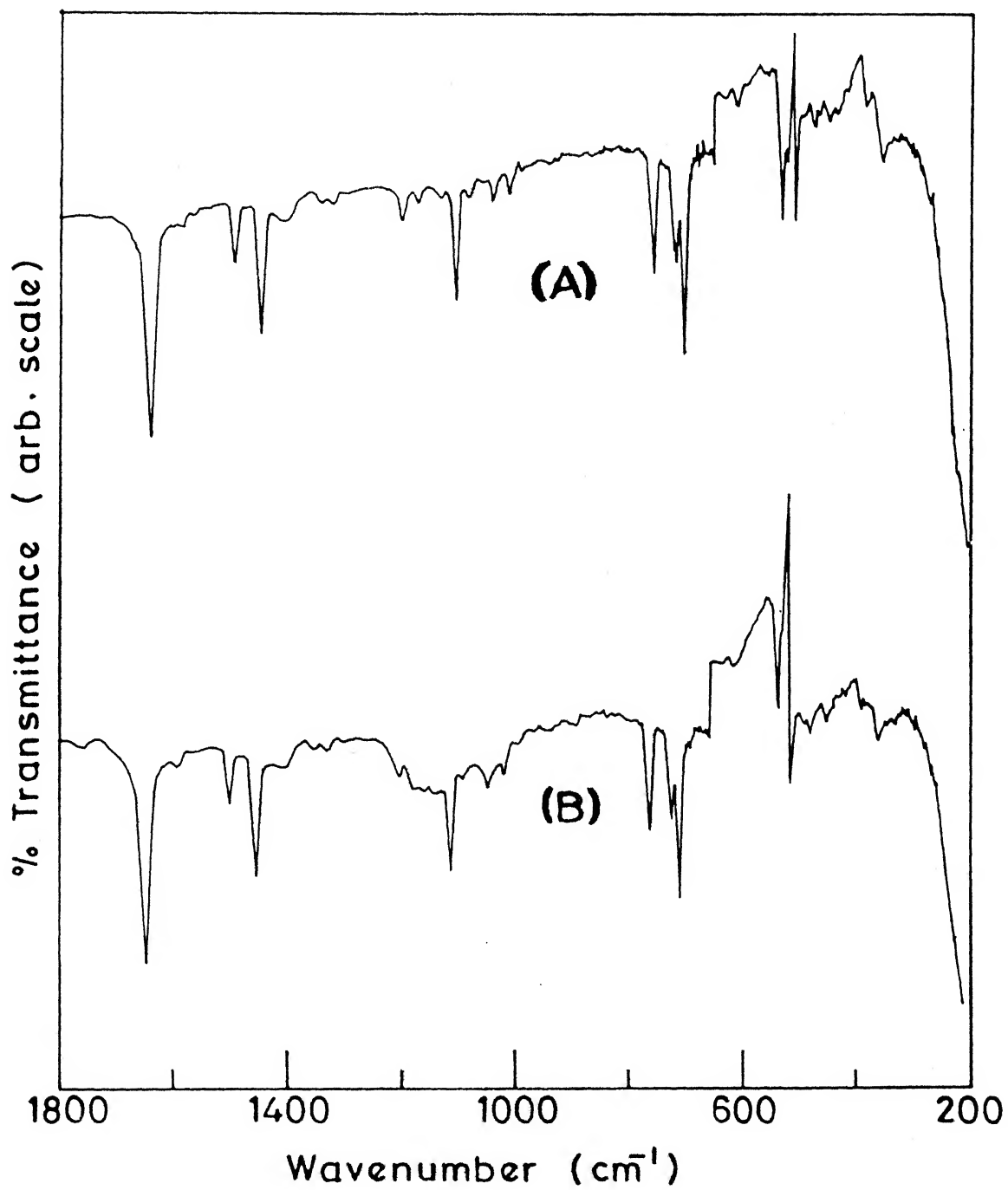
LEGEND TO THE FIGURES

- Fig.II.1 (A)  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$   
 (B)  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$   
 (C)  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$  and  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2]$
- Fig.II.2 (A)  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$   
 (B)  $[\text{Rh}(\text{NO})(\text{PPh}_3)_3]$   
 (C)  $[\text{Rh}(\text{CO})(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$
- Fig.II.3 (A)  $[\text{Ir}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$   
 (B)  $[\{\text{MoCl}_2(\text{PPh}_3)_2\}_2\text{N}_2\text{O}_2]\text{Cl}_2$   
 (C)  $[\text{Co}(\text{en})_2(\text{NO})\text{Cl}]\text{Cl}$



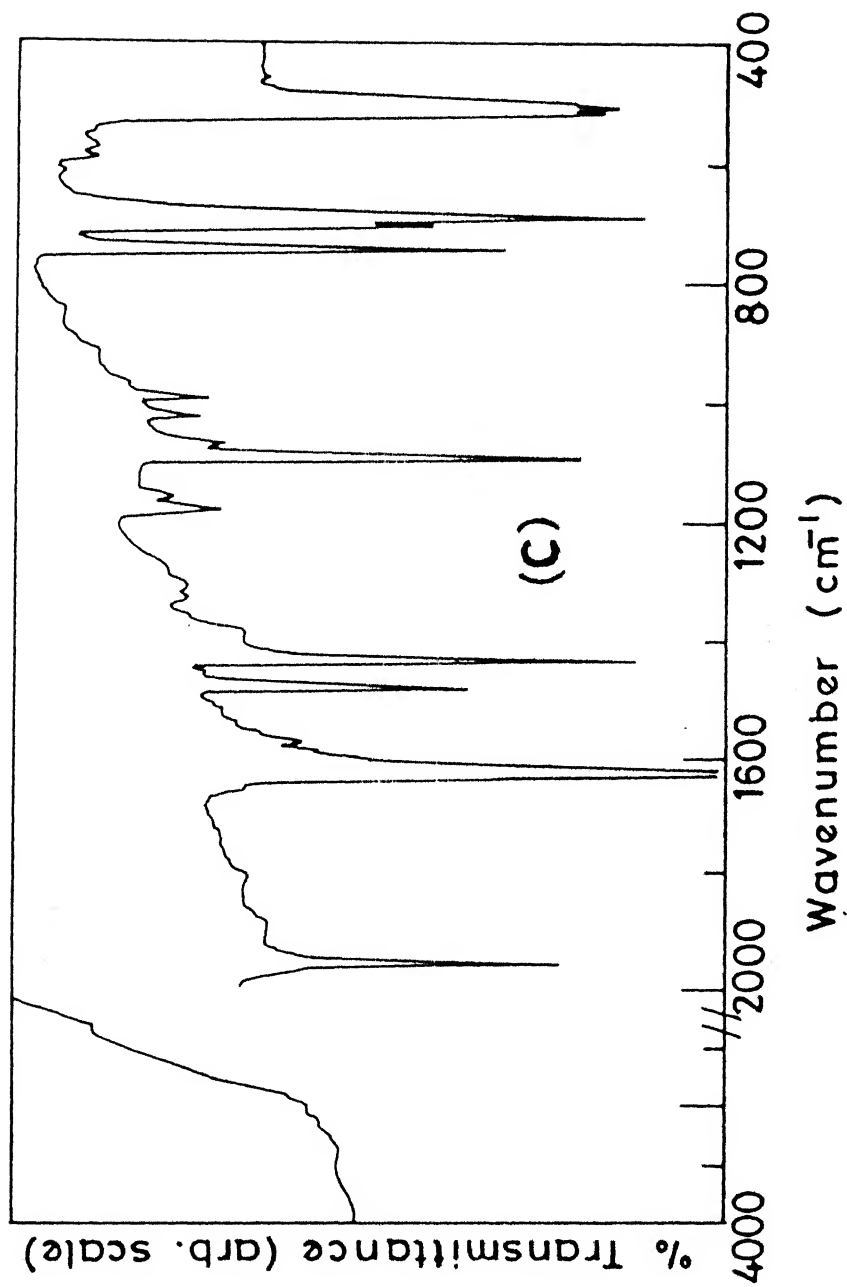
Infrared spectra

FIG. II.1



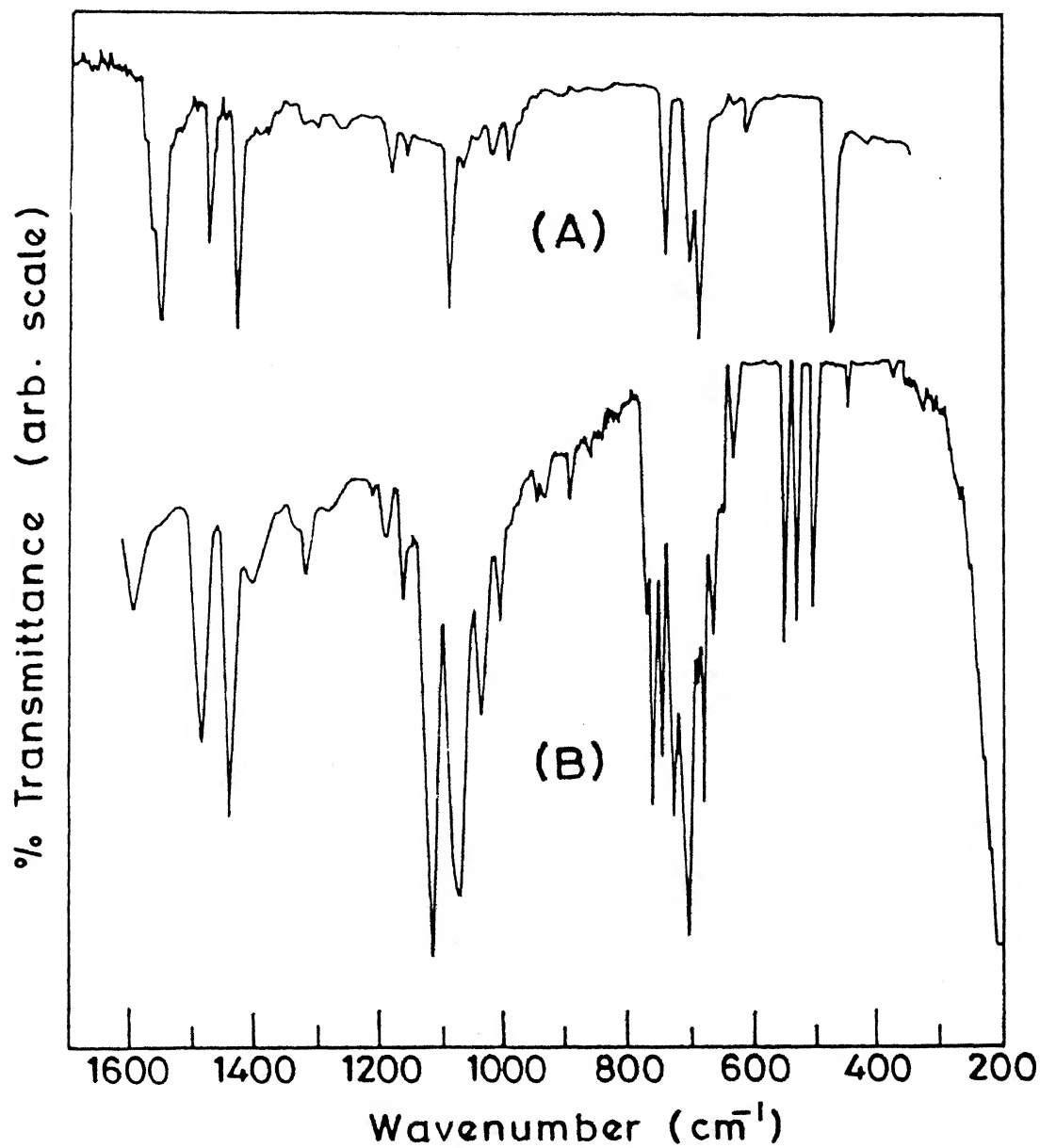
Infrared spectra

FIG. II.2



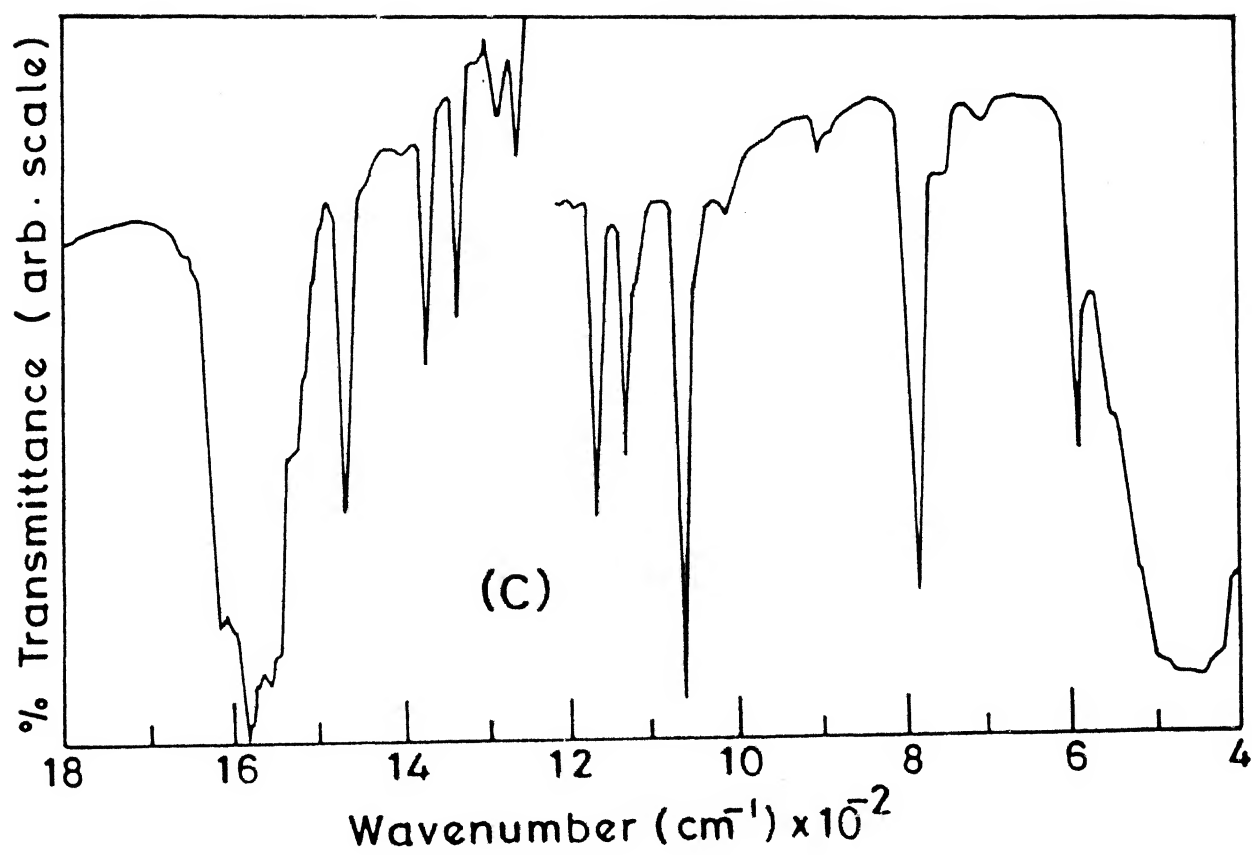
Infrared spectrum

FIG. II.2



Infrared spectra

FIG. II.3



Infrared spectrum

FIG. II.3

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### CHAPTER THREE

#### TRITYL THIONITRITE: A POTENTIAL TRANSFER NITROSATING AGENT FOR METAL NITROSYLATION

In a study relating to the possible transition metal nitrosyl-synthesis, the trans nitrosation has been widely used [1]. A range of transfer nitrosating agents like alkyl nitrites, nitrosamines, NOX ( $X = Cl^-$ ,  $Br^-$ ,  $Br_3^-$ ,  $NO_2^-$ ) have been used for the purpose. In all these systems, the advantage has been taken of the weakness of O-N and N-N bonds. The literature survey, however, indicates practically no work towards in situ trapping of NO by the metal ions generated by weak S-NO bond cleavage, despite their many applications to effect nitrosation of amines and alcohols [2]. These compounds may particularly be suited for such a study because of very large variations in their half lives and decomposition temperature. It is to be of interest to examine trans nitrosation reactions of thionitrites to bring about the thermal addition of NO in metal salts or their complexes, as area of our interest related to the potential use of "In situ trapping of NO" to give a synthetic

route to metal nitrosylation. This chapter concentrates on metal nitrosylation reactions both at high and low temperatures by the denitrosation of trityl thionitrite (hereafter referred as TTN) [3]. The results indicate its use in the synthesis of the literature known nitrosyl complexes, which have been synthesized at higher temperature.

### III.A Experimental

The chemicals used were of Analar grade. TTN and the starting complexes of all the metal ions were prepared and purified by the literature procedures [4-23].

#### III.B.1 Reactions of trityl thionitrite (TTN) with $MCl_3 \cdot xH_2O$ ( $M = Ru, Rh, Ir$ ), $CoCl_2 \cdot 6H_2O$ , $Mo(CO)_6$ in presence of $PPh_3$ , $AsPh_3$ , $SbPh_3$ and ethylenediamine

##### (I) Reaction of TTN with $RuCl_3 \cdot xH_2O$ in presence of triphenylphosphine and dry HCl gas

Solutions of  $RuCl_3 \cdot xH_2O$  (0.5 mmol) in ethanol (10 ml) and TTN (1.0 mmol) in ethanol (10 ml) were added successively to a well stirred boiling solution of triphenylphosphine (2.0 mmol) in ethanol (20 ml). The resulting reaction mixture was heated under reflux for about half an hour. During refluxing a slow stream of dry HCl gas was allowed to pass through the solution intermittantly, whereupon orange yellow crystals were separated. These were filtered, washed

with ethanol, water, ethanol and ether and dried in vacuo. The complex after recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  melted at  $228^\circ\text{C}$ . It was analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ . The same reaction product was obtained when the reaction was carried in presence of  $\text{HgCl}_2$ .

(II) Reaction of TTN with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylarsine

The same procedure as described in [III.B.1(I)] was followed to carry out the reaction except that triphenylarsine was used in place of triphenylphosphine. The product obtained was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , washed with methanol and ether and dried in vacuo. It was analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$  (m.p.  $> 290^\circ\text{C}$ ).

(III) Reaction of TTN with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylstibine

The same procedure as described in [III.B.1(I)] was adopted to carry out the reaction except that triphenylstibine was used in place of triphenylphosphine. The orange red compound, obtained as reaction product, was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , washed with methanol, ether and dried in vacuo (m.p.  $220^\circ\text{C}$ ). It was analysed for  $[(\text{Ru}(\text{NO})-\text{Cl}_3(\text{SbPh}_3)_2)]$ .

(IV) Reaction of TTN with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylphosphine and in the absence of HCl gas or  $\text{HgCl}_2$

The same method as described in [III.B.1(I)] was followed except that reaction was carried out in the absence of HCl gas. The product

obtained was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , washed with methanol, ether and dried in vacuo (m.p.  $>290^\circ\text{C}$ ). It was analysed for  $[\text{Ru}_2(\text{NO})_2\text{Cl}_4\text{S}(\text{PPh}_3)_2]$ .

(V) Reaction of TTN with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylarsine and in the absence of HCl gas or  $\text{HgCl}_2$

The same procedure as described in [III.B.1(I)] was adopted, except that reaction was carried out in the absence of HCl gas and triphenylarsine was used in place of triphenylphosphine. The reaction product was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , washed with methanol and ether and dried in vacuo. It was analysed for  $[\text{Ru}_2(\text{NO})_2\text{Cl}_4\text{S}(\text{AsPh}_3)_2]$ .

(VI) Reaction of TTN with  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylphosphine and HCl gas

Solutions of  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  (0.5 mmol) in ethanol (10 ml) and TTN (1.0 mmol) in ethanol (10 ml) were added to a vigorously stirred boiling solution of triphenylphosphine (2.0 mmol) in (20 ml) ethanol. The resulting reaction mixture was heated under reflux for about half an hour. During the time a slow stream of HCl gas was passed through it whereby orange yellow crystals were separated. These were centrifuged, washed with ethanol, water, ethanol, ether and dried in vacuo. The complex after recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  melted at  $222^\circ\text{C}$  and analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ .

The reaction in the absence of  $\text{HCl}$  or  $\text{HgCl}_2$  yielded the same product, but the yield of the final product was very poor.

(VII) Reaction of TTN with  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylarsine

The same procedure as described in [III.B.1(VI)] was adopted to carry out the reaction except that triphenylarsine was used in place of triphenylphosphine. Crystals obtained after recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  melted at  $245^\circ\text{C}$ . It was analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{AsPh}_3)_2]$ .

(VIII) Reaction of TTN with  $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylphosphine

Solutions of  $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$  (0.5 mmol) in 2-methoxyethanol (10 ml) and TTN (1.0 mmol) in 2-methoxyethanol (10 ml) were added successively to a well stirred solution of triphenylphosphine (2 mmol) in 2-methoxyethanol (20 ml). The resulting reaction mixture was heated under reflux for about half an hour, whereupon a yellow orange crystalline compound separated out. It was centrifuged, washed with ethanol, water, ethanol and ether and dried in vacuo. It melted at  $247^\circ\text{C}$  and was analysed for  $[\text{Ir}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ .

(IX) Reaction of TTN with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in presence of ethylenediamine

A methanolic solution (50 ml) containing (3 mmol) of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and (6 mmol) of TTN was mixed with a methanolic solution (10 ml)

of ethylenediamine (12 mmol). The resulting mixture on heating under reflux for about half an hour afforded an orange micro-crystalline compound. On cooling the solution to room temperature, the crystals were separated by filtration, washed with methanol, ether and dried in vacuo. The compound was analysed for  $[\text{Co(en)}_2\text{-NOCl}]\text{Cl}$ .

(X) Reaction of TTN with  $\text{Mo(CO)}_6$  in presence of triphenylphosphine and chlorine gas

25 ml of warm benzene solution containing  $\text{Mo(CO)}_6$  (0.26 gms, 1 mmol) and TTN (2 mmol) was added to a well stirred boiling benzene solution (25 ml) of triphenylphosphine (5 mmol). The resulting reaction mixture was heated under reflux for about half an hour. During refluxing a slow stream of dry chlorine gas was passed. The refluxing was continued for another half an hour, whereby a pale green coloured compound separated, which was filtered. The compound was extracted with dichloromethane and on adding light petroleum ether to the  $\text{CH}_2\text{Cl}_2$  extract a yellow green compound was separated. It was filtered, washed with petroleum ether and dried in vacuo (m.p.  $165^\circ\text{C}$ ). It was analysed for  $[\{\text{MoCl}_2(\text{PPh}_3)_2\}_2\text{N}_2\text{O}_2]\text{Cl}_2$ .

### III.B.2 Reaction of TTN with the complexes of ruthenium and rhodium

#### (I) Reaction of TTN with $[\text{RuCl}_2(\text{PPh}_3)_3]$ in presence of HCl gas

A solution of TTN (1.5 mmol in dichloromethane (10 ml) was added to a 20 ml hot dichloromethane-ethanol (1:1) solution of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  (0.2 mmol). The resulting reaction mixture was heated under reflux with vigorous stirring. During this time for about two hours a slow stream of dry HCl gas was passed intermittantly through the solution whereupon brown precipitate was separated. After cooling it to room temperature, it was separated by filtration, washed with ethanol, water, ethanol and diethyl ether and dried in vacuo. The shiny crystals of the product melted at  $228^\circ\text{C}$  and was analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ .

The same compound was obtained if the reaction was carried out in presence of  $\text{HgCl}_2$  in place of HCl gas.

#### (II) Reaction of TTN with $[\text{RuCl}_2(\text{PPh}_3)_4]$ in presence of dry HCl gas

The reaction was carried out exactly in the same way as described in [III.B.2(I)] except that  $[\text{RuCl}_2(\text{PPh}_3)_4]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The reaction product after recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  melted at  $228^\circ\text{C}$  and was analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ .

#### (III) Reaction of TTN with $[\text{RuCl}_3(\text{PPh}_3)_2 \cdot \text{MeOH}]$ in presence of HCl gas

The same procedure as described in [III.B.2(I)] was followed

(VII) Reaction of TTN with  $[\text{RuCl}_2(\text{PPh}_3)_3]$  in the absence of HCl gas or  $\text{HgCl}_2$

The reaction was performed by the method described as in [III.B.2(I)] except that it was carried out in the absence of HCl or  $\text{HgCl}_2$ . The product obtained was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , washed with methanol and ether and dried in vacuo. It was analysed for  $[\text{Ru}_2(\text{NO})_2\text{Cl}_4\text{S}(\text{PPh}_3)_2]$ .

(VIII) Reaction of TTN with  $[\text{RuCl}_3(\text{PPh}_3)_2 \cdot \text{MeOH}]$  in the absence of HCl gas or  $\text{HgCl}_2$

The reaction was carried out by the same procedure as described in [III.B.2(I)] except that it was carried out in the absence of HCl or  $\text{HgCl}_2$ . The reaction product was identified as  $[\text{Ru}_2(\text{NO})_2\text{Cl}_4\text{S}(\text{PPh}_3)_2]$ .

(IX) Reaction of TTN with  $[\text{RuCl}_2(\text{PPh}_3)_4]$  in the absence of HCl gas or  $\text{HgCl}_2$

The same reaction procedure was adopted as described in [III.B.2(I)] except that it was carried out in the absence of HCl or  $\text{HgCl}_2$ . The reaction product was identified as  $[\text{Ru}_2(\text{NO})_2\text{Cl}_4\text{S}(\text{PPh}_3)_2]$ .

(X) Reaction of TTN with  $[\text{RuCl}_3(\text{AsPh}_3)_3]$  in presence of HCl gas

The reaction was carried out by the same procedure as described

in [III.B.2(I)] except that  $[\text{RuCl}_3(\text{AsPh}_3)_3]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . Reaction product was recrystallised from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , washed with methanol, ether and dried in vacuo. It was analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$ .

(XI) Reaction of TTN with  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{MeOH}$  in presence of HCl gas

The reaction was performed by the method as described in [III.B.2(I)] except that  $[\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{MeOH}]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The final reaction product was identified as  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$ .

(XII) Reaction of TTN with  $[\text{Ru}(\text{CO})\text{Cl}_2(\text{AsPh}_3)_3]$  in presence of HCl gas

The same procedure as described in [III.B.2(I)] was followed except that  $[\text{Ru}(\text{CO})\text{Cl}_2(\text{AsPh}_3)_3]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The compound obtained as reaction product was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , washed with methanol and ether and dried in vacuo. It was analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$ .

(XIII) Reaction of TTN with  $[\text{Ru}(\text{cp})\text{Cl}(\text{PPh}_3)_2]$  in presence of HCl gas

The reaction was carried out by the same procedure as described in [III.B.2(I)] except that  $[\text{Ru}(\text{cp})\text{Cl}(\text{AsPh}_3)_2]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The reaction product was identified as  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$ .

(XIV) Reaction of  $[\text{RuCl}_3(\text{AsPh}_3)_3]$  with TTN in the absence of  $\text{HgCl}_2$  or  $\text{HCl}$  gas

The reaction was carried out by adopting the same procedure as described in [III.B.2(I)] except that  $[\text{RuCl}_3(\text{AsPh}_3)_3]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  and in the absence of  $\text{HCl}$  gas. The reaction product was identified as  $[\text{Ru}_2(\text{NO})_2\text{Cl}_4\text{S}(\text{PPh}_3)_2]$ .

(XV) Reaction of TTN with  $[\text{RuCl}_3(\text{AsPh}_3)_2\cdot\text{MeOH}]$  in absence of  $\text{HCl}$  gas

The same procedure as described in [III.B.1(I)] was followed except that it was carried out in the absence of  $\text{HCl}$  gas or  $\text{HgCl}_2$  and  $[\text{RuCl}_3(\text{AsPh}_3)_2\cdot\text{MeOH}]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The reaction product was identified as  $[\text{Ru}(\text{NO})\text{Cl}_2\text{S}_{1/2}\text{AsPh}_3]$ .

(XVI) Reaction of TTN with  $[\text{Ru}(\text{CO})\text{Cl}_2(\text{AsPh}_3)_3]$  in the absence of  $\text{HCl}$  gas or  $\text{HgCl}_2$

The same procedure as described in [III.B.2(I)] was adopted to carry out the reaction except that  $[\text{Ru}(\text{CO})\text{Cl}_2(\text{AsPh}_3)_3]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The reaction product was analysed for  $[\text{Ru}_2(\text{NO})_2\text{Cl}_4\text{S}(\text{PPh}_3)_2]$ .

(XVII) Reaction of TTN with  $[\text{RuH}(\text{CO})\text{Cl}(\text{PPh}_3)_3]$  in presence of  $\text{HCl}$  gas or  $\text{HgCl}_2$

The same method as described in [III.B.2(I)] was followed except

that  $[\text{RuH}(\text{CO})\text{Cl}(\text{PPh}_3)_3]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The reaction yielded a shiny yellow crystalline compound, whose analytical and spectral data indicated it to be a mixture of two compounds. Since one of the components was relatively more soluble in benzene, both the components were separated by fractional crystallization using benzene/dichloromethane. The benzene fraction melted at  $228^\circ\text{C}$  and analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$  and the fraction which was crystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  was identified as  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2]$  (m.p.  $233^\circ\text{C}$ ).

(XVIII) Reaction of TTN with  $[\text{RuCl}_2\{(\text{OPh})_3\text{P}\}_4]$  in presence of HCl gas or  $\text{HgCl}_2$

The reaction was performed by the same procedure as described in [III.B.2(I)] except that  $[\text{RuCl}_2\{(\text{OPh})_3\text{P}\}_4]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The reaction product after recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  melted at  $242^\circ\text{C}$  and was analysed for  $[\text{Ru}(\text{NO})\text{Cl}_3\{(\text{OPh})_3\text{P}\}_2]$ .

(XIX) Reaction of TTN with  $[\text{RhCl}(\text{PPh}_3)_3]$  in presence of HCl gas

A solution of TTN (4 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) was added to a red coloured  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  (1:1) solution (10 ml) of  $[\text{RhCl}(\text{PPh}_3)_3]$  (0.2 mmol). The resulting mixture was heated under reflux while passing a slow stream of HCl gas for about half an hour, at the same time, whereupon a red coloured solution was obtained. After cooling it to room temperature, shiny yellow orange crystals were separated. These were separated by filtration, washed with ethanol,

water, ethanol and ether and dried in vacuo. The crystals melted at  $224^{\circ}\text{C}$  and were analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ .

The same reaction product was obtained if the reaction was carried out in the absence of  $\text{HgCl}_2$  or  $\text{HCl}$ , but yield was very poor.

(XX) Reaction of TTN with  $[\text{RhCl}(\text{AsPh}_3)_3]$  in presence of  $\text{HCl}$  gas

The reaction was carried out using the same procedure as described in [III.B.2(XIX)] except that  $[\text{RhCl}(\text{AsPh}_3)_3]$  was used in place of  $[\text{RhCl}(\text{PPh}_3)_3]$ . The reaction product obtained was analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{AsPh}_3)_2]$ .

(XXI) Reaction of TTN with  $[\text{RhCl}(\text{PPh}_3)_2]_2$  in presence of  $\text{HCl}$  gas

The same reaction procedure as described in [III.B.1(XIX)] was followed to carry out the reaction except that  $[\text{RhCl}(\text{PPh}_3)_2]_2$  was used in place of  $[\text{RhCl}(\text{PPh}_3)_3]$ . The reaction product obtained was identified as  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ .

(XXII) Reaction of TTN with  $[\text{RhH}(\text{PPh}_3)_3]$  in presence of  $\text{HCl}$  gas

The reaction was carried out by the same procedure as described in [III.B.2(XIX)] except that  $[\text{RhH}(\text{PPh}_3)_3]$  was used in place of  $[\text{RhCl}(\text{PPh}_3)_3]$ . The reaction product after recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  melted at  $224^{\circ}\text{C}$ , and was analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ .

(XXIII) Reaction of TTN with  $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$  in presence of HCl gas

The same method as described in [III.B.2(XIX)] was adopted to carry out the reaction except that  $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$  was used in place of  $[\text{RhCl}(\text{PPh}_3)_3]$ . The reaction product was analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ .

(XXIV) Reaction of TTN with  $[\text{Rh}(\text{CO})\text{Cl}(\text{AsPh}_3)_2]$  in presence of HCl gas

The same procedure as described in [III.B.2(XIX)] was followed to carry out the reaction except that  $[\text{Rh}(\text{CO})\text{Cl}(\text{AsPh}_3)_2]$  was used in place of  $[\text{Rh}(\text{Cl})(\text{PPh}_3)_3]$ . The reaction product after recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  melted at  $242^\circ\text{C}$  and was analysed for  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{AsPh}_3)_2]$ .

(XXV) Reaction of TTN with  $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$  in presence of HCl gas

The reaction was carried out following the same procedure as described in [III.B.2(XIX)] except that a solution of  $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$  in ethanol (10 ml) was used in place of  $[\text{RhCl}(\text{PPh}_3)_3]$ . The compound obtained as the reaction product melted at  $189^\circ\text{C}$  and was analysed for  $[\text{Rh}(\text{NO})(\text{CO})\text{Cl}_2(\text{PPh}_3)_2]$ .

(XXVI) Reaction of TTN with  $[\text{RhH}\{\text{P}(\text{OPh})_3\}_4]$  in presence of HCl gas

The same method as described in [III.B.2(XIX)] was adopted to carry out the reaction except that  $[\text{RhH}\{\text{P}(\text{OPh})_3\}_4]$  was used in place of  $[\text{RhCl}(\text{PPh}_3)_3]$ . The reaction product was identified as  $[\text{Rh}(\text{NO})\text{Cl}_2\text{P}(\text{OPh})_3]$ .

Reactions of TTN with  $[\text{Pt}(\text{PPh}_3)_4]$ ,  $[\text{Pd}(\text{PPh}_3)_4]$  [35] chromous acetate in presence of diethyldithiocarbamate [36], potassium chromate in presence of ammonium molybdate [37], ammonium heptamolybdate in presence of dithiocarbamate, pyridine and acetyl acetone [38], cobalt(II) chloride in presence of triethyl amine and triphenylphosphine, bipyridyl and lithium perchlorate [39,40], ferrous sulfate in presence of diethyl dithiocarbamate and  $[\text{NiCl}_2(\text{PPh}_3)_2]$  in presence of triphenyl phosphine [41] were carried out by following exactly the literature methods, except that TTN was used as nitrosylating agent.

### III.C Analyses and Physicochemical measurements

Carbon, hydrogen and nitrogen analyses were performed by the Microanalytical section of the Indian Institute of Technology, Kanpur, India. Halide contents in the complexes were determined by the method described elsewhere [24].

I.R. spectra were taken on a Perkin Elmer 580 spectrophotometer in the range 4000–200 using KBr pellets. Melting points and magnetic susceptibilities were recorded on the Fisher-Johns melting point apparatus and Guoy balance at room temperatures respectively. The results are given in Table III.3.

### III.D Results and Discussion

The known thermal instability [25] of TTN allowed the nitrosylation reactions of the metal ions and their complexes. It is obvious from the table that the method has synthetic potential only

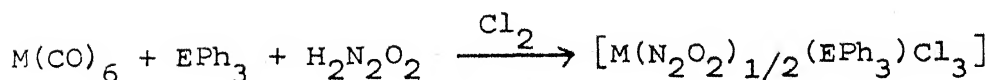
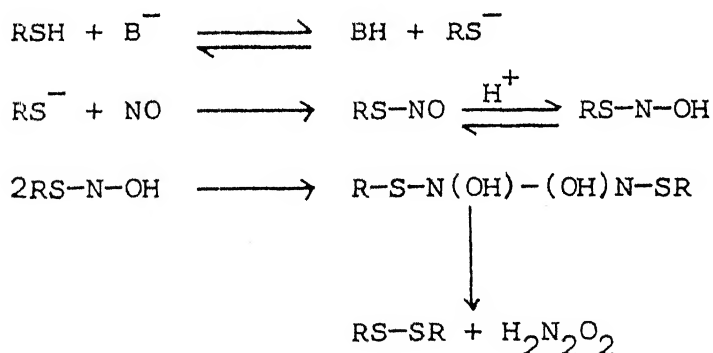
for those metal nitrosyls which are formed and are stable at relatively higher temperatures. The metal nitrosyls which were prepared at room temperature or at low temperatures could not be synthesized using the process of denitrosation of TTN. Since the prepared nitrosyls were known ones, they have been characterized by chemical analyses, and by comparing their colours, melting points, mixed melting points, spectra (i.r., u.v. vis) and magnetic data with those of the authentic complexes.

Table 1 indicates a few reactions which gave unexpected nitrosyl complexes. These are discussed below.

(1) Reaction of  $[\text{RuH}(\text{CO})\text{Cl}(\text{PPh}_3)_3]$  with TTN in presence of either  $\text{HgCl}_2$  or dry  $\text{HCl}$  gas yielded a yellow shiny microcrystalline compound, different from the literature known nitrosyl complex  $[\text{Ru}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]$  [20] prepared by using MNTS. Spectral and analytical data of the product indicated it to be a mixture of two compounds. Its i.r. spectrum exhibited three intense bands at  $1995\text{ cm}^{-1}$  and  $2065\text{ cm}^{-1}$  ( $\nu_{\text{CO}}$ ) and at  $1875\text{ cm}^{-1}$  ( $\nu_{\text{NO}}$ ). The separation of both the complexes were effected by fractional crystallization using benzene/dichloromethane. These were found to be well established complexes viz.,  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$  and  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2]$ . Their identity was supported by analytical and spectroscopic data.

(2) Reactions of  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  with TTN in presence of  $\text{PPh}_3$  or  $\text{AsPh}_3$  and dry chlorine gas yielded compounds having empirical formulae  $[\{\text{MCl}_2(\text{EPh}_3)_2\}_2\text{N}_2\text{O}_2]\text{Cl}_2$  ( $\text{M} = \text{W or Mo}$ ,  $\text{E} = \text{P or As}$ ).

Their i.r. spectra displayed strong bands around  $1145\text{ cm}^{-1}$ ,  $1034\text{ cm}^{-1}$  and  $980\text{ cm}^{-1}$ , which are the characteristic bands for a bridging  $\text{N}_2\text{O}_2^{2-}$  group coordinated through oxygen atoms [26]. A similar reaction of  $\text{Mo}(\text{CO})_6$  with MNTS yielded a dinitrosyl complex [27-28]. The observation, viz., formation of  $\text{N}_2\text{O}_2^{2-}$  complex in place of its dinitrosyl, implied a possibility of the different reaction path. It is well established that in presence of a Lewis base, the denitrosation of thionitrites proceeds with the formation of  $\text{H}_2\text{N}_2\text{O}_2$  [29]. Presuming  $\text{EPh}_3$  acting as a base besides its being a coligand in the present reactions, the generated  $\text{H}_2\text{N}_2\text{O}_2$  interacts with  $\text{M}(\text{CO})_6$  yielding their  $\text{N}_2\text{O}_2^{2-}$  complexes in presence of chlorine gas. The latter may be serving as an oxidant to take Mo from zero to +5 state and a source of chloride ion as well. We tentatively propose the following mechanism,



(M = Mo, W; E = P or As).

The reactions, carried out with other metal ions in presence of  $\text{PPh}_3$ , should also have yielded  $\text{N}_2\text{O}_2^{2-}$  complexes if the  $\text{EPh}_3$

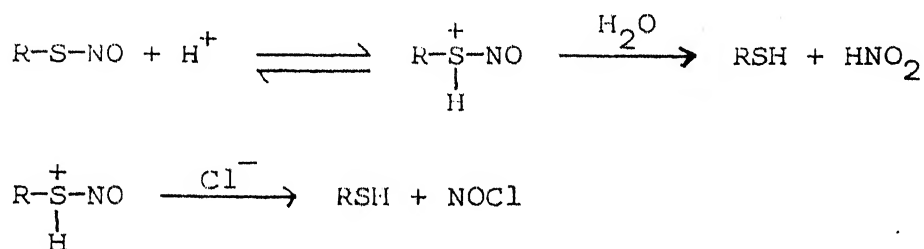
molecules are acting as base. In such cases the relative stability of  $\text{N}_2\text{O}_2^{2-}$  complexes compared to that of nitrosyl ought to be playing an important role in deciding the course of the reaction.

- (3) Reaction of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  with TTN in presence of  $\text{PPh}_3$  or  $\text{AsPh}_3$  in ethanol in the absence of  $\text{HgCl}_2$  or dry  $\text{HCl}$  gas yielded a reddish brown microcrystalline complex with an empirical formula  $[\text{Ru}(\text{NO})\text{Cl}_2\text{S}_{1/2}\text{EPh}_3]$ . These complexes did not melt upto  $300^\circ\text{C}$ . When this complex was heated to reflux with an excess of  $\text{PPh}_3$  or  $\text{AsPh}_3$  in dichloromethane or chloroform it yielded pure  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{EPh}_3)(\text{E}'\text{Ph}_3)]$  ( $\text{E}=\text{E}'=\text{As}$  or  $\text{P}$ ). Ruthenium complexes having  $\text{EPh}_3$  as coligands, on reacting with TTN and in absence of  $\text{HgCl}_2$  or  $\text{HCl}$  gas also yielded the same brown compound.

Reaction of  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  with TTN in presence of  $\text{PPh}_3$ ,  $\text{AsPh}_3$  or  $\text{SbPh}_3$  yielded pure nitrosyl complexes  $[\text{Rh}(\text{NO})\text{Cl}_2\text{L}_2]$  ( $\text{L}=\text{PPh}_3$ ,  $\text{AsPh}_3$  or  $\text{SbPh}_3$ ). The same compounds also obtained in presence of  $\text{HgCl}_2$  or  $\text{HCl}$  gas.

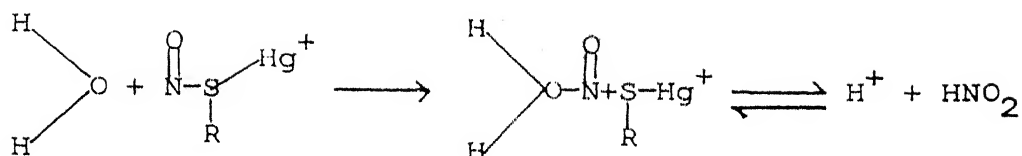
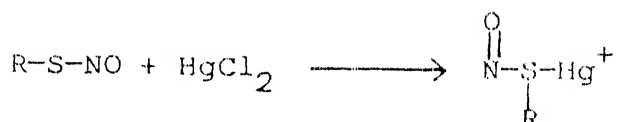
In most of the reactions described, Rh and Ir were introduced in the oxidation state of one while the isolated complexes have the metals in (+3) oxidation state. In these reactions it appears that NO in the complexes is behaving as one electron donor. The formation of the complexes involves probably the oxidation of the metal ion by NO radical or by  $\text{NO}^+$  formed during the heterolytic cleavage of S-N bond which subsequently picks up  $\text{NO}^-$  from the medium to yield  $\text{M}^{+3}$  nitrosyls. Under similar conditions MNTS behaves in an analogous manner.

The thermal homolytic S-N cleavage initially yields NO and thiyl radicals. The latter (thiyl radical) reacts with another molecule of TTN yielding disulfide. It has also been established that in solution the acid catalyzed denitrosation of thionitrites involves the intermediacy of protonated form of thionitrites [30-31].

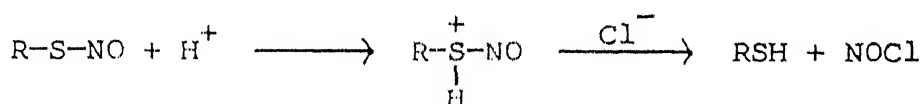


The equilibrium of the above reaction which lies well over to the side of thionitrite may be effectively shifted towards denitrosation of thionitrites by removing free  $\text{HNO}_2$  or  $\text{NOCl}$  as soon as it is formed. Although nitrous acid traps like  $\text{NaN}_3$ , ascorbic acid, urea are well known [32] but it appears that the metal ions or their complexes may also act as scavengers for the nitrous acid or  $\text{NOCl}$  because of their high reactivity towards NO to form their nitrosyls.

In the presence of mercuric chloride, mercuric acetate or silver nitrate the rate of denitrosation reaction is increased to a very large extent [33] which may be rationalized by the following mechanism.



Further it has also been established that the reaction is catalyzed by  $\text{Cl}^-$  ions [34] where the protonated thionitrites react with the chloride ions to give  $\text{NOCl}$ .  $\text{HCl}$  used in the reactions may thus be a good source for both  $\text{H}^+$  and  $\text{Cl}^-$  ions and thereby enhancing the rate of denitrosation of thionitrites yielding  $\text{NOCl}$ .



Although it seems probable that the metal nitrosylation could arise by prior formation of  $\text{HNO}_2$  or  $\text{NOX}$  which subsequently nitrosylate the metal ions, but presently one is not in a position to decide if the reaction is one pot reaction or a multistep one. It seems, however fairly certain that thionitrites can effect nitrosylation of metal ions and compare well with other nitrosylating agents.

Table-1

Reactions carried out and their conditions, products obtained, colour melting point and position  $\gamma_{\text{NO}}$ 

S.No.	Reactants used	Sol-vent	Reaction condition	Specific reaction condition	Reaction Products (colour) (melting point $^{\circ}\text{C}$ )	NO $\gamma_{\text{NO}}$ cm <sup>-1</sup>
1	2	3	4	5	6	7
1.	$\text{RuCl}_3 \cdot x\text{H}_2\text{O} + \text{PPh}_3 + \text{TTN}$ (0.5 mmol) (2 mmol) (1 mmol)	EtOH	Reaction mixture was heated under reflux with stirring for 0.5 hours.	Reaction was carried out in presence of $\text{HgCl}_2$ or dry HCl gas.	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ (0, 228 $^{\circ}\text{C}$ )	1875
2.	$\text{RuCl}_3 \cdot x\text{H}_2\text{O} + \text{AsPh}_3 + \text{TTN}$ (0.5 mmol) (2 mmol) (1 mmol)	-do-	-do-	-do-	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$ (0, did not melt)	1860
3.	$\text{RuCl}_3 \cdot x\text{H}_2\text{O} + \text{SbPh}_3 + \text{TTN}$ (0.5 mmol) (2 mmol) (1 mmol)	-do	-do-	-do-	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$ (OR, 220 $^{\circ}\text{C}$ )	1840
4.	$[\text{RuCl}_2(\text{PPh}_3)_3] + \text{TTN}$ (0.2 mmol) (1.5 mmol)	EtOH/ $\text{CH}_2\text{Cl}_2$	Refluxed for 2 hours with vigorous stirring.	-do-	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ (0, 228 $^{\circ}\text{C}$ )	1875
5.	$[\text{RuCl}_2(\text{PPh}_3)_4] + \text{TTN}$ (0.2 mmol) (1.5 mmol)	-do-	-do-	-do-	-do-	-do-
6.	$[\text{RuCl}_3(\text{PPh}_3)_2 \cdot \text{MeOH}] + \text{TTN}$ (0.2 mmol) (1.5 mmol)	-do-	-do-	-do-	-do-	-do-
7.	$[\text{RuH}_2(\text{PPh}_3)_3] + \text{TTN}$ (0.2 mmol) (1.5 mmol)	-do-	-do-	-do-	-do-	-do-
8.	$[\text{Ru}(\text{cp})\text{Cl}(\text{PPh}_3)_2] + \text{TTN}$	-do-	-do-	-do-	-do-	-do-

2	3	4	5	6	7
$[\text{Ru}(\text{CO})\text{Cl}_2(\text{PPh}_3)_3]$ (0.2 mmol)	+ TTN (1.5 mmol)	-do-	-do-	-do-	-do-
$\text{RuCl}_3 \cdot x\text{H}_2\text{O} + \text{PPh}_3$ (0.5 mmol) (2 mmol) (1 mmol)	+ TTN (1 mmol)	-do-	Reaction was carried out in the absence of $\text{HgCl}_2$ or $\text{HCl}$ gas	$[\text{Ru}(\text{NO})\text{Cl}_2\text{S}_2\text{PPh}_3]$	1800
$[\text{RuCl}_2(\text{PPh}_3)_3]$ (0.2 mmol)	+ TTN (1.5 mmol)	-do-	-do-	-do-	-do-
$[\text{RuCl}_3(\text{PPh}_3)_2 \cdot \text{MeOH}]$ (0.2 mmol)	+ TTN (1.5 mmol)	-do-	-do-	-do-	-do-
$[\text{RuCl}_2(\text{PPh}_3)_4]$ (0.2 mmol)	+ TTN (1.5 mmol)	-do-	-do-	-do-	-do-
$[\text{RuCl}_3(\text{AsPh}_3)_3]$ (0.2 mmol)	+ TTN (1.5 mmol)	-do-	Reaction was carried out in the presence of $\text{HgCl}_2$ or $\text{HCl}$ gas	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$	1860
$[\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{MeOH}]$ (0.2 mmol)	+ TTN (1.5 mmol)	-do-	-do-	-do-	-do-
$[\text{Ru}(\text{CO})\text{Cl}_2(\text{AsPh}_3)_3]$ (0.2 mmol)	+ TTN (1.5 mmol)	-do-	-do-	-do-	-do-
$[\text{Ru}(\text{cp})\text{Cl}(\text{AsPh}_3)_2]$ (0.2 mmol)	+ TTN (1.5 mmol)	-do-	-do-	-do-	-do-

2	3	4	5	6	7
$\text{RuCl}_3 \cdot x\text{H}_2\text{O} + \text{AsPh}_3 + \text{TTN}$ (0.5 mmol) (2.0 mmol) (1 mmol)	EtOH	-do-	Reaction was carried out in the absence of $\text{HgCl}_2$ or HCl gas	$[\text{Ru}(\text{NO})\text{Cl}_2\text{S}_{1/2}(\text{AsPh}_3)]$	180
$[\text{RuCl}_3(\text{AsPh}_3)_3] + \text{TTN}$ EtOH/ $\text{CH}_2\text{Cl}_2$	-do-	-do-	-do-	-do-	-do-
$[\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{MeOH} + \text{TTN}$ (0.2 mmol) (1.5 mmol)	-do-	-do-	-do-	-do-	-do-
$[\text{Ru}(\text{CO})\text{Cl}_2(\text{AsPh}_3)_3] + \text{TTN}$ (0.2 mmol) (1.5 mmol)	-do-	-do-	-do-	-do-	-do-
$[\text{RuH}(\text{CO})\text{Cl}(\text{PPh}_3)_3] + \text{TTN}$ (0.2 mmol) (1.5 mmol)	EtOH	-do-	Reaction was carried out in presence of $\text{HgCl}_2$ or HCl gas	$[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ (0, 228°C)	1875
				+	
				$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2]$ (0, 233°C)	1990 2065
$[\text{RuCl}_2\{\text{P}(\text{OPh})_3\}_4] + \text{TTN}$ (0.2 mmol) (1.5 mmol)	EtOH/ $\text{CH}_2\text{Cl}_2$	-do-	-do-	$[\text{Ru}(\text{NO})\text{Cl}_3\{\text{P}(\text{OPh})_3\}_2]$ (Y, 242°C)	1900
$[\text{RhCl}_3 \cdot x\text{H}_2\text{O} + \text{PPh}_3 + \text{TTN}$ (0.5 mmol) (2 mmol) (1 mmol)	EtOH	-do-	-do-	$[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$	1630
$[\text{RhCl}_3 \cdot x\text{H}_2\text{O} + \text{AsPh}_3 + \text{TTN}$	-do-	-do-	-do-	$[\text{Rh}(\text{NO})\text{Cl}_2(\text{AsPh}_3)_2]$ (0, 245°C)	1625

2	3	4	5	6	7
	EtOH/ CH <sub>2</sub> Cl <sub>2</sub>				
$[\text{RhCl}(\text{AsPh}_3)_3 + \text{TTN}]$ (0.2 mmol) (1.5 mmol)		-do-	-do-	-do-	-do-
$[\text{RhCl}(\text{PPh}_3)_3] + \text{TTN}$ (0.2 mmol) (1.5 mmol)	-do-	-do-	-do-	$[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$	1630
$[\text{RhCl}(\text{PPh}_3)_2]_2 + \text{TTN}$ (0.2 mmol) (1.5 mmol)	-do-	-do-	-do-	-do-	-do-
$[\text{RhH}(\text{PPh}_3)_3] + \text{TTN}$ (0.2 mmol) (1.5 mmol)	-do-	-do-	-do-	-do-	-do-
$[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2] + \text{TTN}$ (0.2 mmol) (1.5 mmol)	-do-	-do-	-do-	-do-	-do-
$[\text{Rh}(\text{CO})\text{Cl}(\text{AsPh}_3)_2] + \text{TTN}$ (0.2 mmol) (1.5 mmol)	-do-	-do-	-do-	$[\text{Rh}(\text{NO})\text{Cl}_2(\text{AsPh}_3)_2]$ (0, 245°C)	1625
$[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ (0.2 mmol) (1.5 mmol)	-do-	-do-	-do-	$[\text{Rh}(\text{NO})(\text{CO})\text{Cl}_2(\text{PPh}_3)_2]$ (0, 189°C)	1630, 1965
$[\text{Rh}\{\text{P}(\text{OPh})_3\}_4] + \text{TTN}$	-do-	-do-	-do-	$[\text{Rh}(\text{NO})\text{Cl}_2\{\text{P}(\text{OPh})_3\}_2]$ (0, )	1635
$[\text{IrCl}_3 \cdot x\text{H}_2\text{O} + \text{PPh}_3 + \text{TTN}]$ (0.5 mmol) (2 mmol) (1 mmol)	2 methoxy Ethanol	-do-	-do-	$[\text{Ir}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ (OX, 247°C)	1555

$[\text{CoCl}_2 \cdot 6\text{H}_2\text{O}] + \text{en} + \text{TTN}$ (3mmol) (12mmol) (6mmol)	MeOH	-do-	-do-	$[\text{Co(en)}_2(\text{NO})\text{Cl}]\text{Cl}$ (0 -	1630
$[\text{Mo}(\text{CO})_6]^+ + \text{PPh}_3 + \text{TTN}$ (1 mmol) (6 mmol) (2 mmol)	Benzene	-do-	Slow stream of $\text{Cl}_2$ stream was passed through the solution	$\{\text{MoCl}_2(\text{PPh}_3)_2\}_2$ $\text{N}_2\text{O}_2[\text{Cl}_2$ (YG - 165°C)	1145, 1034, 980
$[\text{W}(\text{CO})_6]^+ + \text{PPh}_3 + \text{TTN}$ (2 mmol) (6 mmol) (2 mmol)	-do-	-do-	-do-	$[\{\text{WCl}_2(\text{PPh}_3)_2\}_2$ $\text{N}_2\text{O}_2[\text{Cl}_2$	-do-
$[\text{Pt}(\text{PPh}_3)_4] + \text{TTN}$ <sup>(35)</sup> (1 mmol) (2 mmol)	Benzene	Stirred at room tempera- ture for 24 hours	-do-	Nitrosyl(hyponi- tritel) complex could not be obtained	-
$[\text{Pd}(\text{PPh}_3)_4] + \text{TTN}$ (1 mmol) (2 mmol)	Benzene	-do-	-do-	-do-	-
$[\text{Cr}(\text{II})\text{acetate} + \text{dte} + \text{TTN}$ <sup>(36)</sup> (1mmol) (2mmol) (1mmol)	Ethanol	Reaction mixt- ure was stirred at °C for 3 hours.	-do-	Nitrosyl compound could not be obtained	-
$\text{K}_2\text{Cr}_2\text{O}_4 + \text{NH}_4\text{SCN} + \text{TTN}$ <sup>(37)</sup> (2.5mmol) (25mmol) (36 mmol)	$\text{H}_2\text{O} +$ Methanol	Reaction mixture was heated for 1.5 hours in presence of Zn	-do-	-do-	-
$\text{K}_2\text{Cr}_2\text{O}_7 + \text{NH}_4\text{SCN} + \text{TTN}$	-do-	-do-	-	-do-	-

2	3	4	5	6	7
$K_2Cr_2O_4 + NH_4SCN + TTN+dtc$	-do-	-do-	-	-do-	
(38) $(NH_4)_6Mo_7O_{24} \cdot 4H_2O + TTN + Py$ (1mmol) (2 mmol) Pyridine/ Acetic acid mixture		Reaction mixture was heated at 80°C for one hour, then diluted with 250 ml of $H_2O$ & conc. HCl was added			Mitrosyl complexes could not be obtained
(39) $(NH_4)_6Mo_7O_{24} \cdot 4H_2O + TTN$ (1 mmol) (2 mmol) DMF		Reaction mixture heated for 1 hour at 80°C & sodium salt of itc was added with stirring after cooling		-do-	
(40) $(NH_4)_6Mo_7O_{24} \cdot 4H_2O + TTN$ (1 mmol) (2 mmol) DMF		Reaction mixture heated at 80°C for one hour After cooling acac was added		-do-	
(41) $CoCl_2 \cdot 6H_2O + LiClO_4 + Bipy+TTN$ (.2 gm) (.2gm) (.37gm)(.58 gm)	-do-	Reaction mixture was stirred for 3 hours at room temperature		-do-	
(42) $CoCl_2 \cdot 6H_2O + LiClO_4 + NaNO_2 + TTN$ (.2gm) (.2gm) (.1gm) (.58 gm)	-do-			-do-	
(43) $CoCl_2 \cdot 6H_2O + PPh_3 + TTN + Et_3N$	Ethanol	Reaction mixture was stirred for .5 hours		-do-	

2	3	4	5	6	7
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$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ + dtc + TTN (1mmol) (2 mmol) (2 mmol)	Ethanol	Stirred with cooling for more than 1-2 hours	-	-do-	
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$\text{NiCl}_2(\text{PPh}_3)_2$ + $\text{PPH}_3$ + TTN <sup>(41)</sup> (.67mmol) (.67mmol) (11.5mmol)	THF	Reaction mixture was refluxed for .5 hours	-	-do-	
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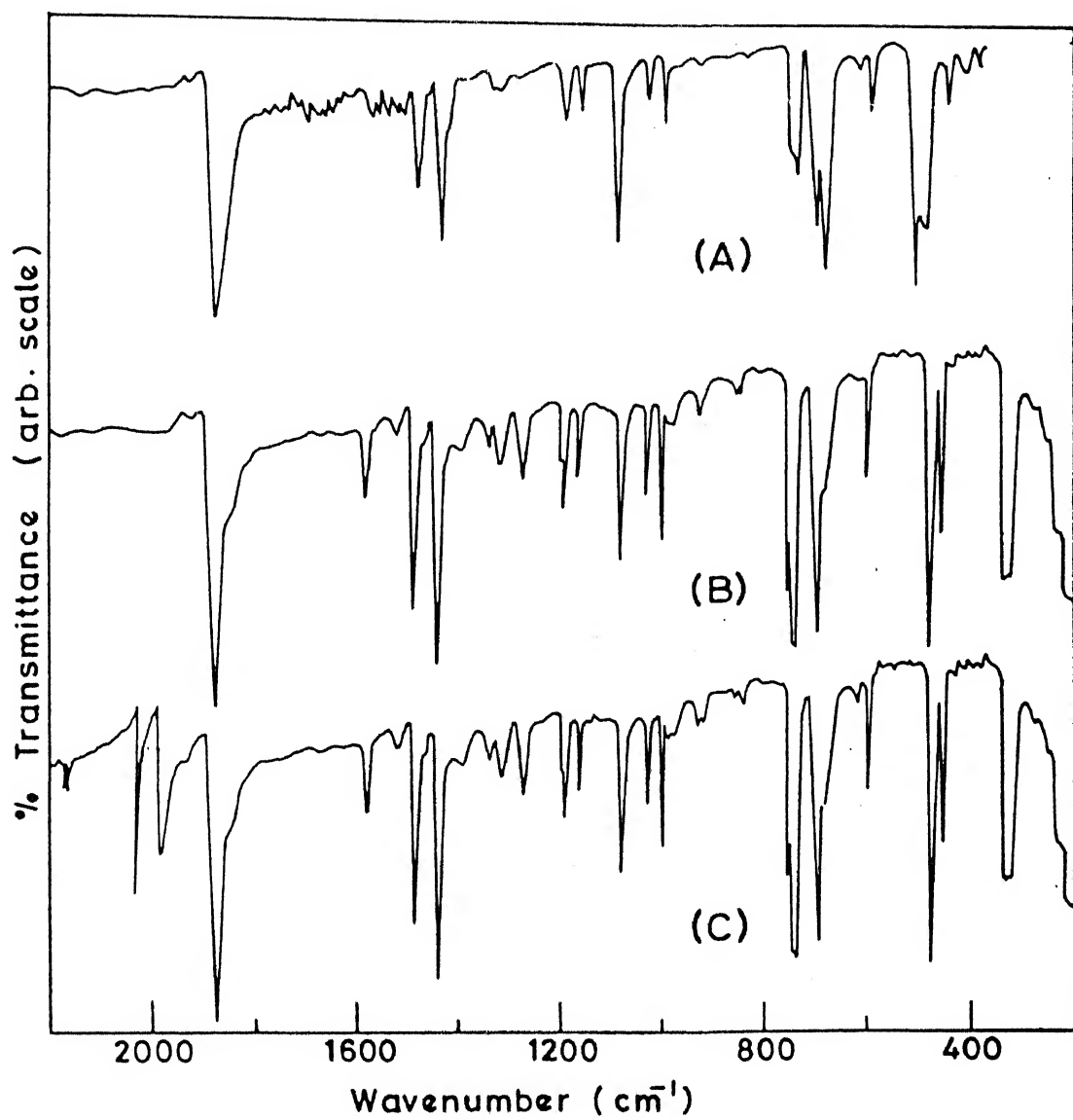
ange; OR=orange red; RB=red brown; B=brown; Y=yellow; Y3=yellow green; dtc=diethyldithiocarbamate;  
 pyridine; bipy=2,2'-bipyridyl; acac=acetylacetone.

LEGEND TO THE FIGURES

- Fig.III.1 (A)  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$   
 (B)  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$   
 (C)  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$  and  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2]$   
 (D)  $[\text{Ru}(\text{NO})\text{Cl}_2\text{S}_{1/2}(\text{PPh}_3)]$

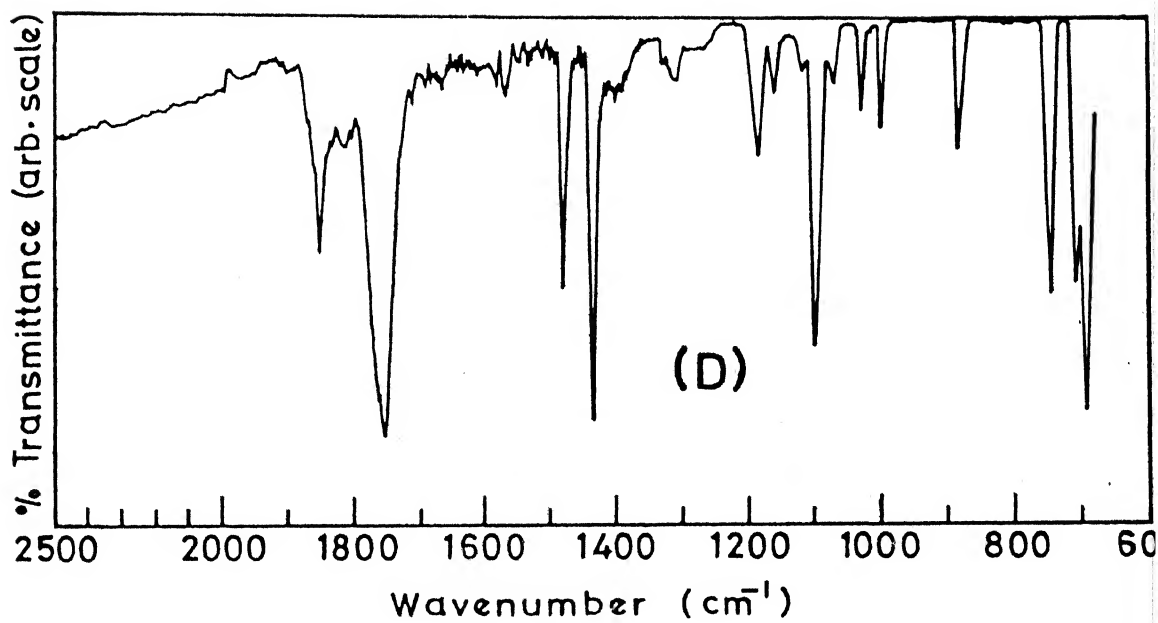
- Fig.III.2 (A)  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$   
 (B)  $[\text{Rh}(\text{NO})(\text{PPh}_3)_3]$   
 (C)  $[\text{Rh}(\text{CO})(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$

- Fig.III.3 (A)  $[\text{Ir}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$   
 (B)  $[\{\text{MoCl}_2(\text{PPh}_3)_2\}_2\text{N}_2\text{O}_2]\text{Cl}_2$   
 (C)  $[\{\text{WCl}_2(\text{PPh}_3)_2\}_2\text{N}_2\text{O}_2]\text{Cl}_2$



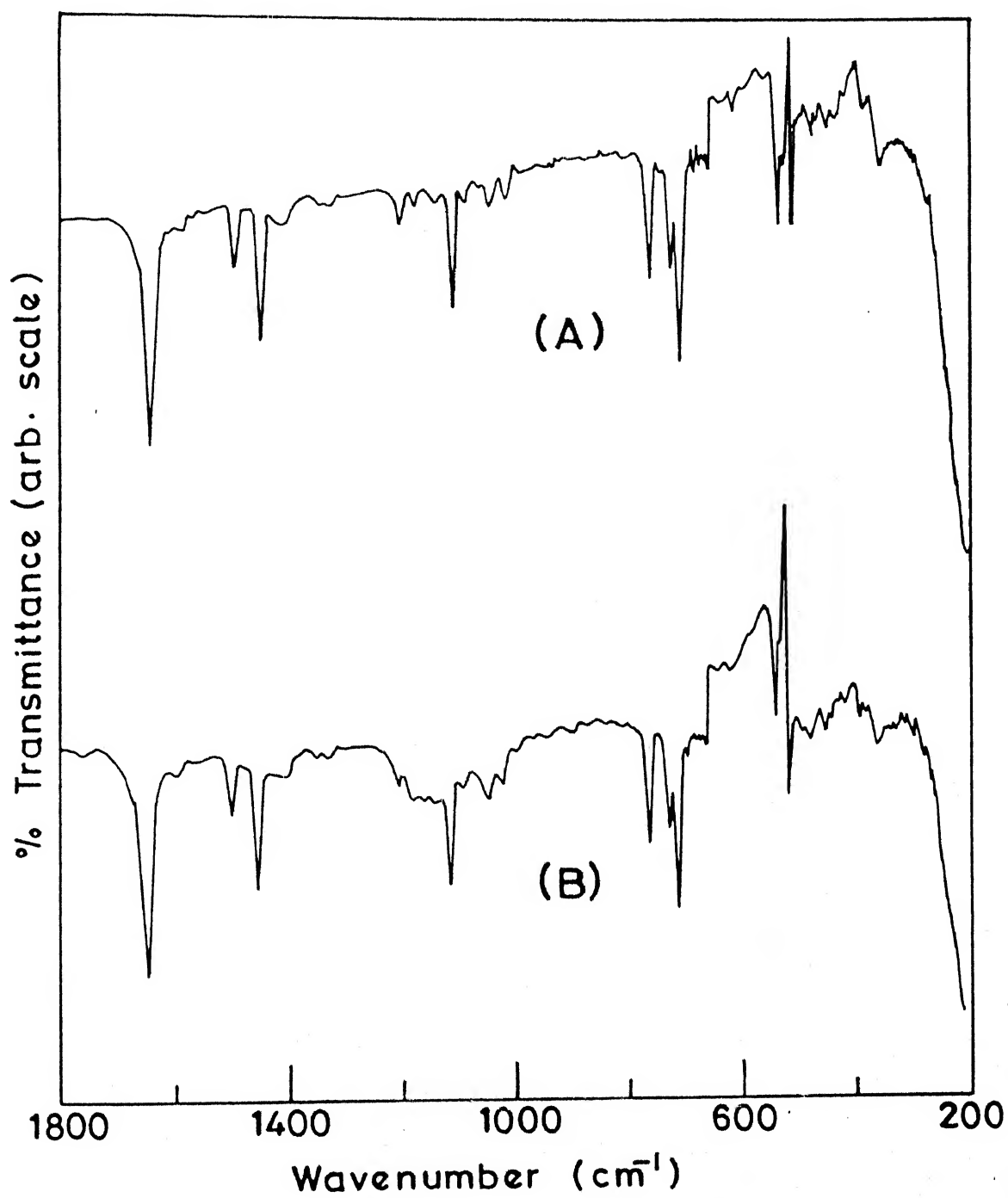
Infrared spectra

FIG. III.1



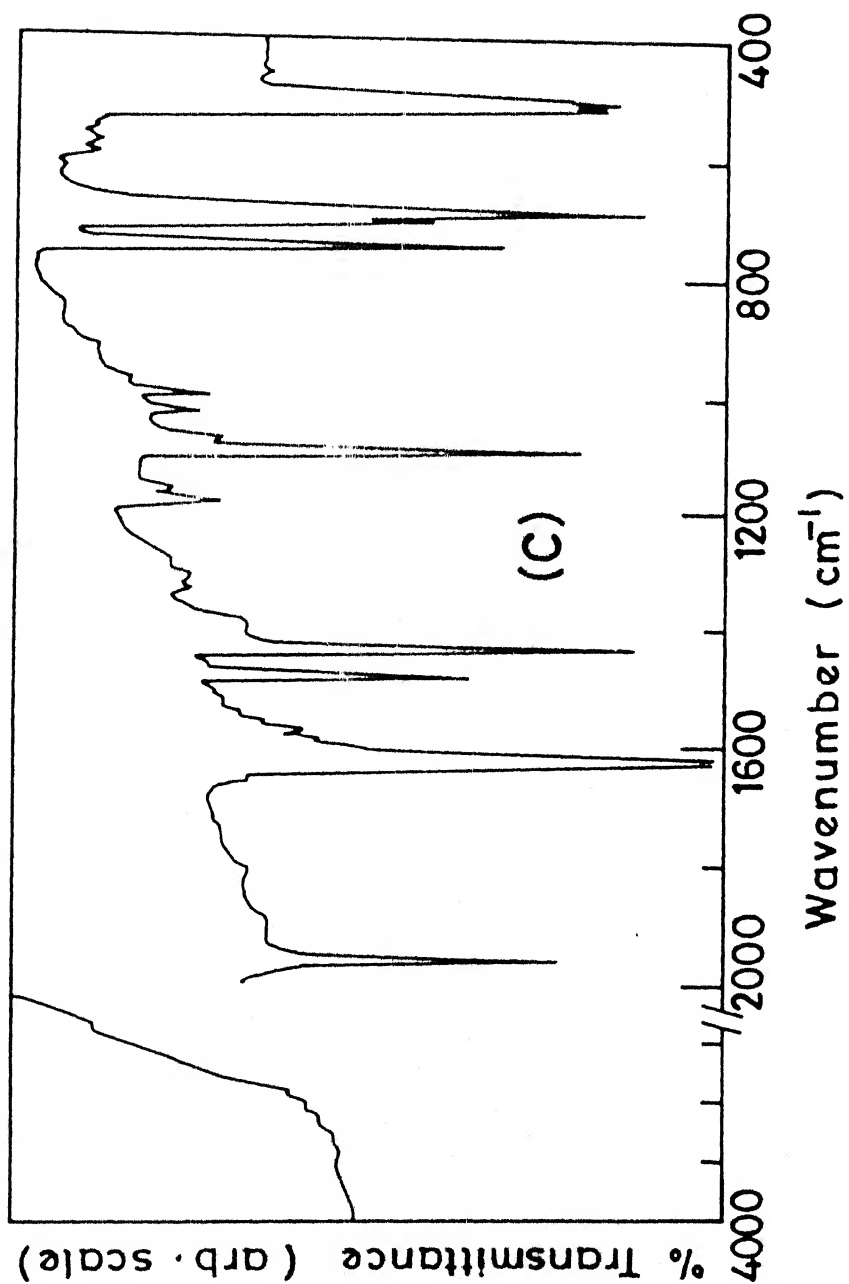
Infrared spectrum

FIG. III.1



Infrared spectra

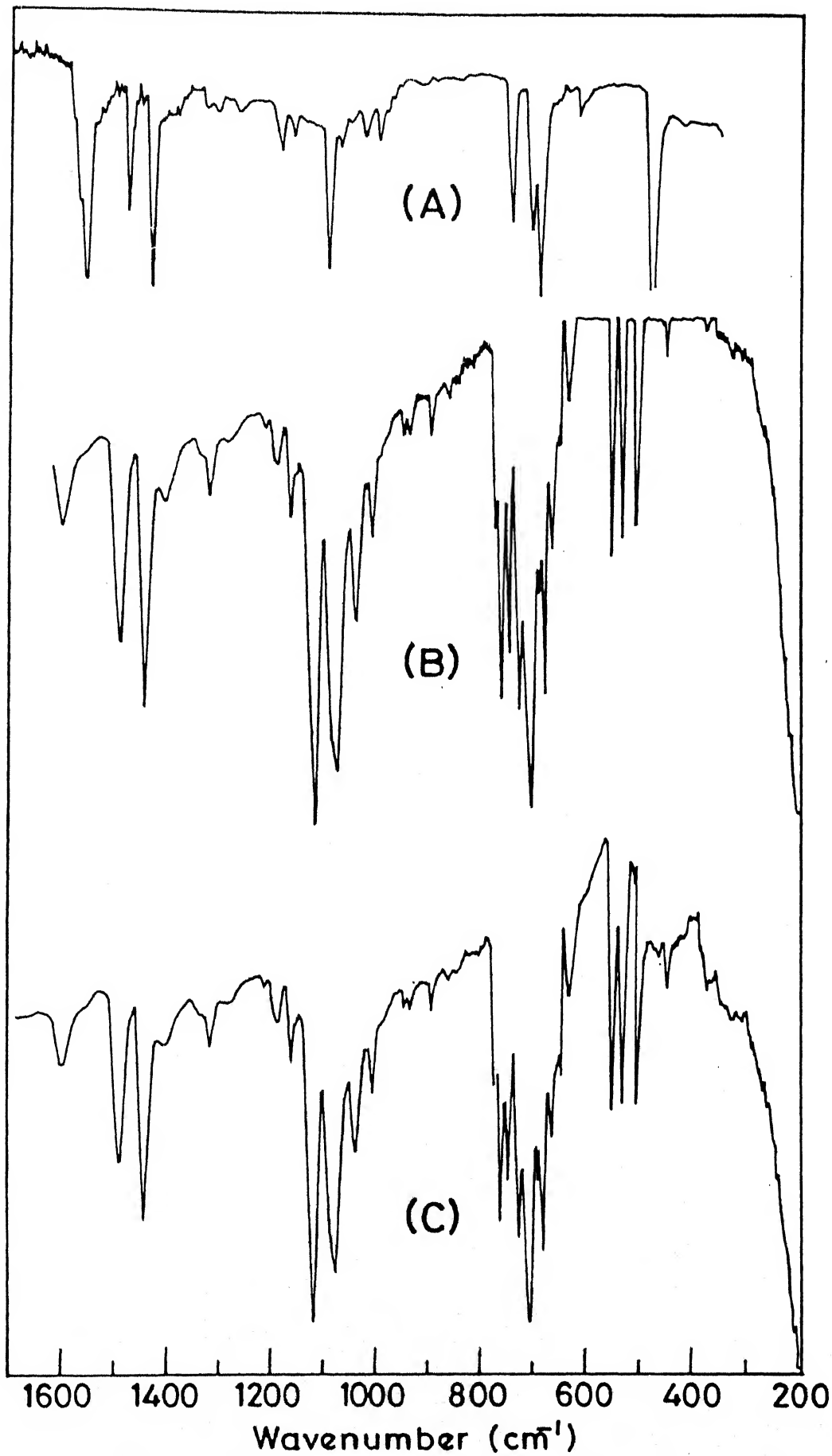
FIG.III.2



Infrared spectrum

FIG. III.2

% Transmittance (arb. scale)



Wavenumber ( $\text{cm}^{-1}$ )

Infrared spectra

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## CHAPTER FOUR

### IN SITU TRAPPING OF NO: APPLICATION OF S-NITROSO DERIVATIVES FOR METAL NITROSYLS SYNTHESIS

In situ trapping of NO as a synthetic procedure for metal-nitrosyls using N-nitroso derivatives ( $\begin{smallmatrix} R \\ \diagdown \\ N-NO \\ \diagup \\ R \end{smallmatrix}$ ) has been exploited in our earlier work [1] and an attempt was made there to generalize the method and to reduce multistep process for nitrosyl synthesis to a single-step one. It was also pointed out that the reactivity of a particular N-nitroso derivatives is a function of the substituents R and R'.

Because of our continuing interest in finding new procedures for metal nitrosylation, we looked into the possibility of employing recently synthesized S-nitroso derivatives [2] as nitrosylating agents which undergo dissociation reaction ( $2 \text{ RS-NO} \longrightarrow \text{R-S-S-R} + 2 \text{ NO}$ ) at varying temperatures depending upon the organic moiety linked to the sulfur. The temperature dependence of S-nitroso

derivatives has further added an interest in us because for most of the cases the percentage yield of a particular metal nitrosyl using NO as a nitrosylating agent is temperature dependent. (Some metal nitrosyls can not be synthesized even at room temperature)[3]. Thus there exists a possibility of choosing a S-nitroso derivative for a particular metal nitrosyl synthesis. The focus of this chapter is to study the nitrosyl group transfer in solution from S-nitrosocysteine to metal centers (Ru, Rh, Co) in presence of other coligands.

#### IV.A Experimental

Chemically pure grade chemicals were used throughout. S-nitrosocysteine [4,5] and starting complexes of Ru and Rh were prepared and purified by literature procedures [6,7].

#### IV.B Synthetic Procedure

##### (I) Reaction of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ with S-Nitrosocysteine in the presence of Triphenylphosphine

40 ml of a solution containing (25 ml) of ethanolic solution of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (0.5 mmol), triphenylphosphine (2 mmol), (15 ml) of S-nitrosocysteine (0.48 mmol) in tris solution was heated under reflux for 40-45 min, whereupon shining yellow crystals of  $[\text{Ru}(\text{cys-cys})_2\text{Cl}(\text{NO})]$  were separated on cooling the solution. Crystals were filtered, washed with water, ethanol and dried under vacuum.

(II) Reaction of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  with S-Nitrosocysteine

15 ml of an aqueous solution of S-nitrosocysteine (0.48 mmol) was added to (10 ml) ethanolic solution of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  (0.05 mmol) and the reaction mixture was heated to reflux for 40-45 min whereby a yellowish orange coloured compound  $[\text{Ru}(\text{NO})\text{Cl}_2(\text{cys-cys})(\text{PPh}_3)_2]$  was separated. It was filtered and washed as in (I) and dried in vacuum.

(III) Reaction of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  with S-Nitrosocysteine in presence of  $\text{HgCl}_2$

The procedure for carrying out the reaction was the same as that given in (II) except that 0.05g of  $\text{HgCl}_2$  was added to the reaction mixture. It resulted in the formation of a compound which was analyzed as  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ .

(IV) Reaction of  $[\text{RuCl}_2(\text{PPh}_3)_4]$  with S-Nitrosocysteine

5 ml of an aqueous solution of S-nitrosocysteine was allowed to react with (10 ml) of an ethanolic solution of  $[\text{RuCl}_2(\text{PPh}_3)_4]$  by the procedure given in (II) whereupon  $[\text{Ru}(\text{NO})\text{Cl}_2(\text{cys-cys})(\text{PPh}_3)]$  was precipitated out.

(V) Reaction of  $[\text{RhCl}(\text{PPh}_3)_3]$  with S-Nitrosocysteine

A solution of  $[\text{RhCl}(\text{PPh}_3)_3]$  (0.1 mmol) in (15 ml) of ethanol was allowed to react with (15 ml) of an aqueous solution of s-nitroso-

cysteine (0.5 mmol), according to the procedure given in (II) whereby  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)(\text{cys-cys})]$  was separated.

The same reaction when carried out in presence of  $\text{HgCl}_2$  yielded  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ .

(VI) Reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with S-Nitrosocysteine in presence of  $\text{LiClO}_4$  and 2,2'-Bipyridyl

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.25g) and  $\text{LiClO}_4$  (0.2g) were dissolved in (20 ml) of absolute ethanol and the solution was deaerated by flushing with nitrogen. A solution of 2,2'-bipyridyl (0.37g) dissolved in hot ethanol (10 ml) was slowly added to the  $\text{CoCl}_2$  solution under nitrogen, followed by the addition of S-nitrosocysteine (0.25g) in (15 ml) water. The resulting solution was stirred at room temperature for 30 minutes, whereby brown microcrystalline compound  $[\text{Co}(\text{bipy})_2\text{Cl}(\text{NO})]\text{ClO}_4$  was separated. It was filtered, washed with ethanol, ether and dried under vacuum.

(VII) Reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with S-Nitrosocysteine in the presence of  $\text{LiClO}_4$ ,  $\text{NaNO}_2$ , and 2,2'-Bipyridyl

0.15g 2,2'-bipyridyl, (0.5g)  $\text{LiClO}_4$ , and (0.04g)  $\text{NaNO}_2$  were mixed in 10 ml of ethanolic solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.15g) and deaerated with  $\text{N}_2$  gas, followed by the addition of 15 ml of S-nitrosocysteine solution in water. The colour of the solution turned brown and finally a yellowish brown solid was separated out. It was filtered,

washed with ethanol and ether and dried under vacuum. The compound was analyzed for  $[\text{Co}(\text{bipy})_2(\text{NO})(\text{NO}_2)]\text{ClO}_4$ .

#### IV.C Analyses and physicochemical measurements

Microanalytical work has been carried out in the Microanalytical Lab. of the Indian Institute of Technology, Kanpur. Infra-red spectra have been recorded on a Perkin-Elmer 580 Spectrophotometer in KBr discs. Magnetic measurements were made on a Guoy balance at room temperature. The results are given in Table IV.1.

#### IV.D Results and Discussion

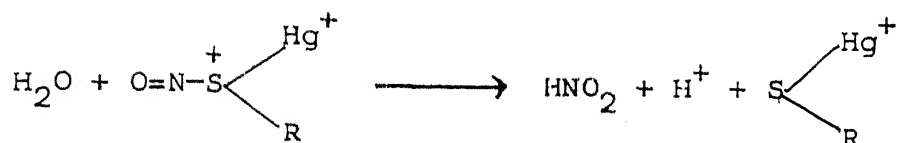
The empirical formulae of the compounds resulting by the interaction of S-nitrosocysteine with metal ions are enlisted in Table IV.1. The bright yellow diamagnetic Ru(II) complex  $[\text{RuCl}(\text{NO})(\text{cys-cys})_2]$  exhibited in its IR spectrum a band at  $1870\text{ cm}^{-1}$  corresponding to  $(\nu_{\text{NO}})$  besides the characteristic bands of cystine. The positions of all cystine bands (3500, 2900, 2565, 1742, 1577, 1521, 1231, 1216 and  $876\text{ cm}^{-1}$ ) except one around  $1700\text{ cm}^{-1}$  (assigned to  $(\nu_{\text{CO}})$  of  $\text{COO}^-$  group) remained constant. The lowering of  $1700\text{ cm}^{-1}$  band position suggested bonding of ruthenium through  $\text{COO}^-$  moiety. Presuming ruthenium in +2 oxidation state with a formal charge of +1 on NO  $[(\nu_{\text{NO}}), 1870\text{ cm}^{-1}]$  the charge balance required cystine to be bonded with ruthenium as uninegative ion (Dipositive ruthenium in the complex is also suggested by its diamagnetic nature). It is

therefore, assumed that the binding of cystine with ruthenium occurs through COOH group after deprotonation. Further six being the preferred coordination number of Ru(II) in its complexes [8] each cystine anion should provide two bonding sites to the metal center which could be either another oxygen, sulfur or nitrogen atom. Although it is difficult to decide the second donor site, but since the positions of other IR bands assigned to cystine remained practically unaltered, we tentatively assume oxygen atom of the  $\text{COO}^-$  group to be another bonding site. It is, however, only tentative.

An orange yellow complex having an empirical formula  $[\text{RuCl}_2^-(\text{NO})(\text{PPh}_3)_2(\text{cys-cys})]$  has been obtained by the reaction of  $[\text{RuCl}_2^-(\text{PPh}_3)_3]$  with S-nitrosocysteine. The IR spectrum exhibited the characteristic bands of  $\text{PPh}_3$  and cystine. The position of  $(\nu_{\text{CO}})$  of cystine also shifted to lower wave number suggesting the bonding of ruthenium with carboxyl group after deprotonation because of the charge balance as discussed in the preceding paragraph.

It appears that in both Ru(II) complexes cited above, cystine formed during the decomposition of S-nitrosocysteine also coordinated to ruthenium along with NO group. In order to inhibit the cystine coordination during the reaction, a strategy of removing the cystine from the reaction site formed after decomposition of S-nitroso compound was thought. If the reaction is performed in presence of  $\text{HgCl}_2$ , the latter will not only catalyze the decomposition of S-nitroso compound [9] but will also pickup preferentially

the formed organothio radical leaving NO radical for coordination with the metal ion in accordance with the following reaction:



Thus, the reaction when carried out in the presence of excess  $\text{HgCl}_2$  yielded pure  $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$  in our reactions.

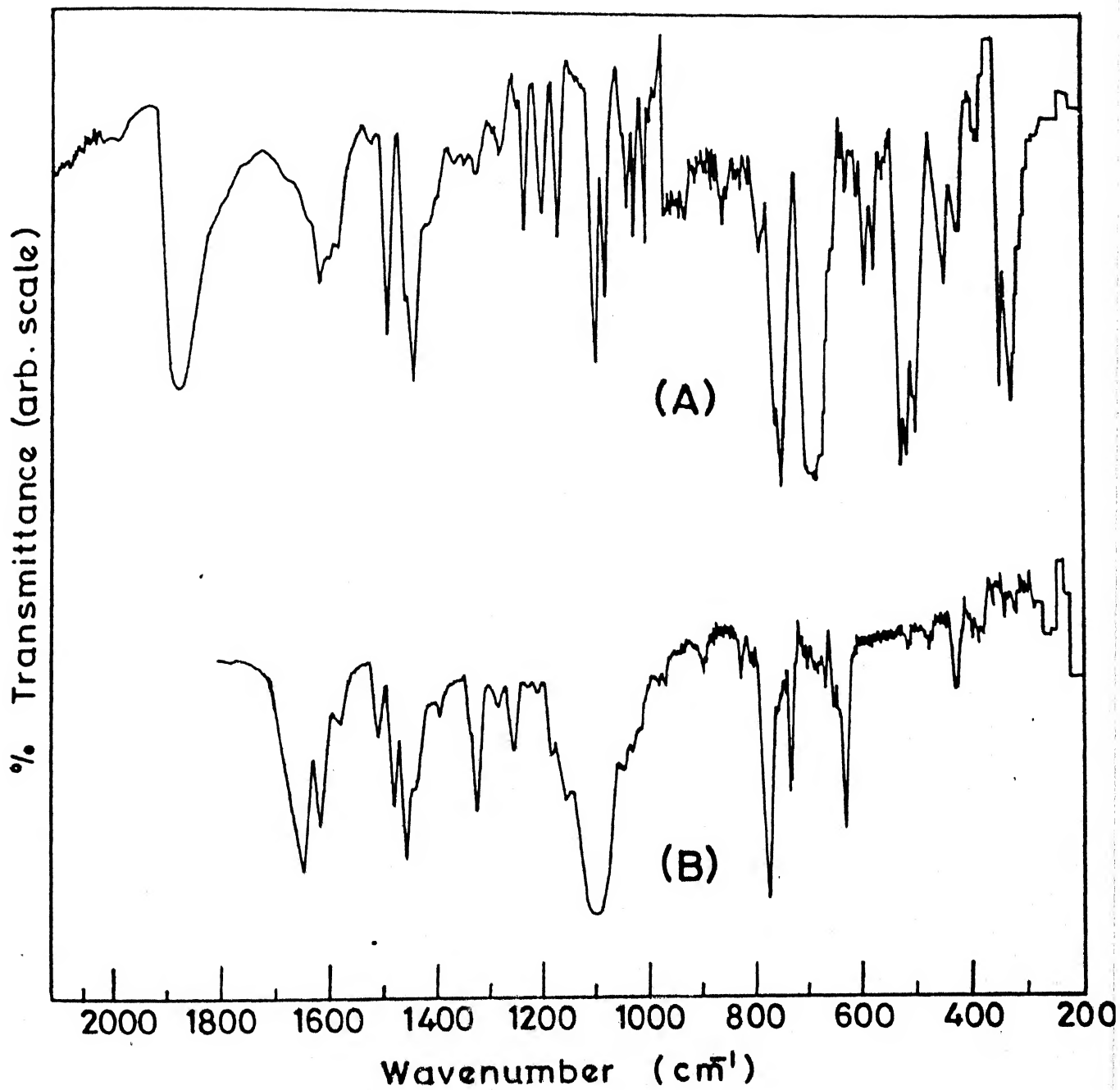
Similar to ruthenium complexes the reaction of  $[\text{RhCl}(\text{PPh}_3)_3]$  with S-nitrosocysteine yielded a mixture of  $[\text{RhCl}_2(\text{NO})(\text{PPh}_3)(\text{cys-cys})]$  and  $[\text{RhCl}_2(\text{NO})(\text{PPh}_3)_2]$ . However, the same reaction in presence of  $\text{HgCl}_2$  yielded pure literature known compound  $[\text{RhCl}_2(\text{NO})(\text{PPh}_3)_2]$ .

The reaction of Co(II) salts with the S-nitroso compound did not yield a complex having bonded cystine even under varying reaction conditions. These reactions, however, yielded pure literature known complexes (Table 1). Possibly Co(II), being 'a' class metal ions may not bind preferentially with sulfur-containing cystine in presence of a better base, viz 2,2'-bipyridyl. The literature known complexes viz.  $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$  [10],  $[\text{RhCl}_2(\text{NO})(\text{PPh}_3)_2]$  [11],  $[\text{CoCl}(\text{NO})(\text{bipy})_2]\text{ClO}_4$  [12],  $[\text{Co}(\text{NO}_2)(\text{NO})(\text{bpy})_2]\text{ClO}_4$  [12] were identified by comparing their m.p. mixed m.p. spectral (IR, UV, and visible) and magnetic properties with the authenticated samples prepared by the literature methods.

It is evident from the above discussion that there exists a definite possibility of applying successfully S-nitrosocysteine, in particular, and S-nitroso derivatives, in general, for metal nitrosylation reactions. It is also obvious that the competitive reaction of the generated organothio radical to link with the metal ion (particularly b-class) along with its dimerization can be inhibited by adding excess  $\text{HgCl}_2$  which not only assists in removing the thio radical from the reaction but also catalyzes the decomposition of S-nitroso compounds. Further work in this direction is in progress where the application of the method will be utilized for the nitrosylation of other metal ions with other S-nitroso derivatives, especially those having stability at low temperature. The latter reactions will be carried out with those metal ions where nitrosyls are obtained only at low temperature.

Table IV.1. Analytical Data of the Complexes

Compound	Analysis: Calcd (Found)/				
	C	H	N	X	S
$[\text{RuCl}(\text{NO})(\text{cys-cys})_2]\cdot\text{H}_2\text{O}$	21.6 (21.8)	3.6 (4.1)	10.5 (10.5)	5.4 (4.8)	19.2 (21.5)
$[\text{RuCl}_2(\text{NO})(\text{PPh}_3)_2(\text{cys-cys})]$	52.2 (53.9)	4.3 (4.1)	4.3 (4.5)	7.1 (7.7)	6.4 (6.5)
$[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$	56.9 (55.7)	4.1 (3.0)	2.0 (1.9)	14.3 (14.0)	- -
$[\text{RhCl}_2(\text{NO})(\text{PPh}_3)_2]$	59.3 (58.7)	4.1 (3.8)	1.9 (2.3)	9.7 (10.4)	- -
$[\text{RhCl}_2(\text{NO})(\text{cys-cys})(\text{PPh}_3)]$	-	-	-	-	-
$[\text{CoCl}(\text{NO})(\text{bipy})_2]\text{ClO}_4$	44.8 (44.8)	3.0 (3.1)	13.0 (12.7)	12.8 (11.8)	- -
$[\text{Co}(\text{NO})(\text{NO}_2)(\text{bipy})_2]\text{ClO}_4$	42.7 (42.9)	2.8 (3.1)	14.9 (14.7)	6.2 (6.3)	- -



Infrared spectra

FIG. IV.1

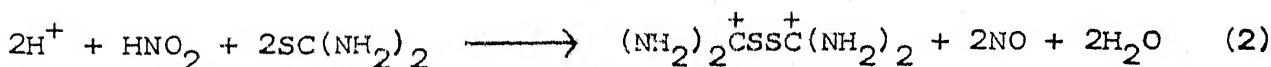
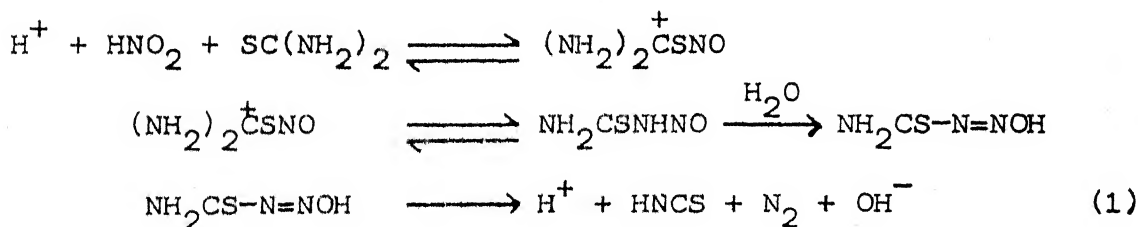
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## CHAPTER FIVE

### NITROSTHIOUREA: ITS REACTIVITY WITH METAL IONS AND THEIR COMPLEXES

The studies of Werner [1] and Stedman, et al. [2] have shown that the unstable S-nitrosothiourothonium ion formed by the reaction of  $\text{HNO}_2$  with thiourea undergoes dissociation through two parallel pathways (1) and (2).



The first mechanism which proceeds via initial migration of the nitroso group from sulphur to nitrogen with the subsequent hydrolysis of N-nitroso product to thiocyanic acid and  $\text{N}_2$ , is favoured at low acidities, while the second one, at higher acidities. In

both the parallel reactions, NO group is either generated (2) or migrated from sulphur to nitrogen(1). A possibility arises that S-nitrosothiourothonium ion (referred hereafter as NTU) might act as a nitrosylating agent because of the generation of NO group in both the pathways, which might be trapped by a metal ion, if present in the system, to form its metal nitrosyl. However the formation of NCS ion may create a problem in its own right. This, being a very good ambidentate ligand, may preferentially be picked up by the metal ions to yield thiocyanato complexes. Since in situ trapping of NO, by metal ions lies within our interest, we have set out to examine the reactivity of NTU as nitrosylating agent over a range of acidities (from 2M to pH 7). In addition, metal ions chosen for the reactions are those which form metal nitrosyls at room or at low temperature. Since these metal ions can also be potential thiocyanate scavengers, the relative overall efficacy of NO group trapping by the metal ions to that of thiocyanate ions under given experimental conditions may also be compared. This chapter reports some work in this direction.

#### V.A Experimental

The chemicals used were of Analar or chemically pure grade. Solvents were freshly distilled. NTU, complexes of Ru, Rh, Ir, Pd and Pt were prepared and purified by the literature methods [3-7].

V.B.1 Reactions of nitrosothiourea (NTU) with Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Ag(I), Zn(II), Cd(II) and Hg(II) salts in presence of pyridine, 2,2'-bipyridyl and 1,10-phenanthroline

(I) Reaction of NTU with Co(II) acetate in presence of pyridine

25 ml methanolic solution containing Co(II) acetate (1 mmol) was cooled to about  $0^{\circ}\text{C}$  using an ice-salt bath. 15 ml aqueous solution of NTU (freshly prepared) and (4.5 mmol) of pyridine were simultaneously added to this with vigorous stirring. The stirring of the resulting solution was further continued for about half an hour more at zero degree, whereupon a pink compound separated. It was filtered, washed with water and methanol. It was extracted with excess of alcohol and the deep blue extract was slowly evaporated on a water bath whereby pink needle shaped crystals were crystallized out. These were filtered, washed with ether and dried in vacuo. They were analysed for  $[\text{Co}(\text{py})_3(\text{NCS})_2]$ .

(II) Reaction of NTU with Cr(II) acetate in presence of pyridine

The same procedure as described in [V.B.1(I)] was adopted to carry out the reaction except that Cr(II) acetate was used in place of Co(II) acetate. The reaction product was washed with water, ethanol and dried in vacuo. It was analysed for  $[\text{Cr}(\text{py})_3(\text{NCS})_2 \cdot \text{H}_2\text{O}]$ .

(III) Reaction of NTU with Mn(II) chloride in presence of pyridine

The same method as described in [V.B.1(I)] was followed except

that Mn(II) chloride was used in place of Co(II) acetate. The reaction product was identified as  $[\text{Mn}(\text{py})_4(\text{NCS})_2] \cdot \frac{1}{2}\text{MeOH}$ .

(IV) Reaction of NTU with Fe(II) sulfate in presence of pyridine

The reaction was carried out following the same procedure as described in [V.B.1(I)] except that Fe(II) sulfate was used in place of Co(II) acetate. The brownish black needles which were obtained as the reaction product, analysed for  $[\text{Fe}(\text{py})_4(\text{NCS})_2]$ .

(V) Reaction of NTU with Ni(II) chloride in presence in pyridine

The same reaction procedure as described in [V.B.1(I)] was adopted to carry out the reaction except that Ni(II) chloride was used in place of Co(II) acetate. The final reaction product which was obtained, analysed for  $[\text{Ni}(\text{py})_4(\text{NCS})_2]$ .

(VI) Reaction of NTU with Cu(II) sulfate in presence of pyridine

The procedure adopted to carry out the reaction was the same as described in [V.B.1(I)] except that Cu(II) sulfate was used in place of Co(II) acetate. The reaction product was identified as  $[\text{Cu}(\text{py})_4(\text{NCS})_2]$ .

(VII) Reaction of NTU with  $\text{AgNO}_3$  in presence of pyridine

The same method as described in [V.B.1(I)] was followed to carry

out the reaction except that  $\text{AgNO}_3$  was used in place of  $\text{Co(II)}$  acetate. The white needle shaped crystals, obtained as the reaction product, were analysed for  $[\text{Ag(py)}_2(\text{NCS})_2]$ .

(VIII) Reaction of NTU with  $\text{ZnCl}_2$  in presence of pyridine

The same procedure as described in [V.B.1(I)] was adopted to carry out the reaction except that  $\text{ZnCl}_2$  was used in place of  $\text{Co(II)}$  acetate. The reaction product was analysed for  $[\text{Zn(py)}_3(\text{NCS})_2 \cdot \text{H}_2\text{O}]$ .

(IX) Reaction of NTU with  $\text{CdSO}_4$  in presence of pyridine

The reaction was carried out by the procedure as described in [V.B.1(I)] except that  $\text{CdSO}_4$  was used in place of  $\text{Co(II)}$  acetate  $[\text{Cd(py)}_2(\text{NCS})_2]$  was the reaction product.

(X) Reaction of NTU with  $\text{HgCl}_2$  in presence of pyridine

The reaction was performed by the method as described in [V.B.1(I)] except that  $\text{HgCl}_2$  was used in place of  $\text{Co(II)}$  acetate. White crystals of the  $[\text{Hg(py)}_2(\text{SCN})_2]$  were obtained as the reaction product.

(XI) Reaction of  $\text{Co(II)}$  Acetate with NTU in presence of 2,2'-bipyridyl

A methanolic solution (25 ml) of  $\text{Co(II)}$  acetate (1 mmol) was added to 10 ml of NTU solution (freshly prepared) containing 2 mmol

of bipyridyl. The resulting mixture was stirred at  $0^{\circ}\text{C}$  for half an hour, whereupon a bluish pink compound was separated out. It was filtered, washed with water, methanol and dried in vacuo. The compound was analysed for  $[\text{Co}(\text{bipy})_2(\text{NCS})_2]$ .

(XII) Reaction of NTU with Co(II) Acetate in presence of 1,10-phenanthroline

The same procedure as described in [V.B.1(XI)] was adopted to carry out the reaction except that 1,10-phenanthroline was used in place of 2,2'-bipyridyl. The reaction product was analysed for  $[\text{Co}(\text{bipy})_2(\text{NCS})_2]$ .

(XIII) Reaction of NTU with Ni(II) Nitrate in presence of 2,2'-bipyridyl

The reaction was carried out by the same procedure as described in [V.B.1(XI)] except that Ni(II) nitrate was used in place of Co(II) chloride. The blue needle shaped crystals, obtained as the reaction product, were analysed for  $[\text{Ni}(\text{bipy})_2(\text{NCS})_2]$ .

(XIV) Reaction of NTU with Ni(II) Nitrate in presence of 1,10-phenanthroline

The procedure adopted to carry out the reaction was same as

described in[V.B.1(XII)]except that Ni(II) nitrate was used in place of Co(II) acetate. The reaction product was identified as  $[\text{Ni}(\text{phen})_2(\text{NCS})_2]$ .

(XV) Reaction of NTU with Cu(II) sulfate in presence of 2,2'-bipyridyl

The reaction was carried out following the same procedure as described in[V.B.1(XI)]except that Cu(II) sulfate was used in place of Co(II) acetate. The greenish needles which were obtained as the reaction product analysed for  $[\text{Cu}(\text{bipy})_2(\text{NCS})_2]$ .

(XVI) Reaction of NTU with Cu(II) Sulfate in presence of 1,10-phenanthroline

The same method as described in[V.B.1(XII)]was followed to carry out the reaction except that Cu(II) sulfate was used in place of Co(II) acetate. The green needle shaped crystal were analysed for  $[\text{Cu}(\text{phen})_2(\text{NCS})_2]$ .

V.B.2 Reaction of  $[\text{Co}(\text{py})_3(\text{NCS})_2]$  with tetramethyl, tetraethyl and tetrabutyl ammonium chloride

(I) Reaction of  $[\text{Co}(\text{py})_3(\text{NCS})_2]$  with  $[(\text{CH}_3)_4\text{N}]^+\text{Cl}$

20 ml of a methanolic solution containing (1 mmol) of  $[\text{Co}(\text{py})_3(\text{NCS})_2]$  was added to a 10 ml methanolic solution of  $[(\text{CH}_3)_4\text{N}]^+\text{Cl}$  (2.0 mmol). The resulting mixture was heated under reflux for about an hour. On cooling it to room temperature and concentrating it to nearly half its volume on a water bath, a deep blue oily product was separated which on repeated crystallization from  $\text{CH}_2\text{Cl}_2$  afforded a deep blue complex. It was filtered, washed with alcohol, ether and dried in vacuo. It was analysed for  $[(\text{CH}_3)_4\text{N}]_2[\text{CoCl}_2(\text{NCS})_2]$ .

(II) Reaction of  $[\text{Co}(\text{py})_3(\text{NCS})_2]$  with  $[(\text{C}_2\text{H}_5)_4\text{N}]^+\text{Cl}$

The same reaction procedure was followed as described in [V.B.2(I)] except that  $[(\text{C}_2\text{H}_5)_4\text{N}]^+\text{Cl}$  was used in place of  $[(\text{CH}_3)_4\text{N}]^+\text{Cl}$ . The reaction product was analysed for  $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{CoCl}_2(\text{SCN})_2]$ .

(III) Reaction of  $[\text{Co}(\text{py})_3(\text{NCS})_2]$  with  $[(\text{C}_4\text{H}_9)_4\text{N}]^+\text{Cl}$

The same method as described in [V.B.2 .(1)] was followed to carry out the reaction except that  $[(\text{C}_4\text{H}_9)_4\text{N}]^+\text{Cl}$  was used in place of  $[(\text{CH}_3)_4\text{N}]^+\text{Cl}$ . The reaction product was identified as  $[(\text{C}_4\text{H}_9)_4\text{N}]_2[\text{Co}(\text{SCN})_4]$ . The yield was relatively poor.

### V.B.3 Reaction of NTU with Ru, Rh, Ir, Pd and Pt complexes

#### (I) Reaction of NTU with $[\text{RuCl}_2(\text{PPh}_3)_3]$

15 ml solution of NTU (freshly prepared) was added to a refluxing solution containing (.260)gms of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  in 25 ml, 1:1 ethanol/ $\text{CH}_2\text{Cl}_2$ . The resulting mixture was refluxed for about 1.5 hours. On cooling the solution to room temperature, a yellow orange microcrystalline compound was precipitated. It was separated by filtration, washed with ethanol, and diethyl-ether and dried in vacuo. It was repeatedly recrystallized from  $\text{CH}_2\text{Cl}_2$ /petroleum ether, washed with petroleum ether and analysed for  $[\text{Ru}(\text{NO})(\text{NCS})_2(\text{PPh}_3)_2\text{Cl}] \frac{1}{2} \text{CH}_2\text{Cl}_2$ .

#### (II) Reaction of NTU with $[\text{RhCl}(\text{PPh}_3)_3]$

The same reaction procedure was followed as described in [V.B.3 (I)] except that  $[\text{RhCl}(\text{PPh}_3)_3]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ .  $[\text{Rh}(\text{NO})(\text{NCS})\text{Cl}(\text{PPh}_3)_3]$  was obtained as the reaction product.

#### (III) Reaction of NTU with $[\text{IrCl}_3(\text{PPh}_3)_3]$

The reaction was carried out by the procedure as described in [V.B.3(I)] except that  $[\text{IrCl}_3(\text{PPh}_3)_3]$  was used in place of  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . The reaction product was repeatedly recrystallized from  $\text{CH}_2\text{Cl}_2$ /MeOH. A pale yellow crystalline complex  $[\text{Ir}(\text{PPh}_3)_2(\text{NCS})_2\text{Cl}(\text{thiourea})]$  was separated as the reaction product.

(IV) Reaction of NTU with  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 

The same method as described in V.B.I.(I) was followed to carry out the reaction except that  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  was used in place of Co(II) acetate. The reaction was carried out in absence of pyridine. The yellow crystalline compound which was obtained as the reaction product was analysed for  $[\text{Ru}(\text{NCS})(\text{NO})(\text{NH}_3)_4]\text{Cl}_2$ .

(V) Reaction of NTU with  $[\text{Pd}(\text{PPh}_3)_4]$ 

The same reaction procedure as described in [V.B.I(I)] was followed except that it was carried out in the absence of pyridine. 25 ml solution of  $[\text{Pd}(\text{PPh}_3)_4]$  in ethanol/dichloromethane (1:1) was used in place of Co(II) acetate. The final reaction product was analysed for  $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$ .

(VI) Reaction of NTU with  $[\text{Pt}(\text{PPh}_3)_4]$ 

The procedure adopted to carry out the reaction was the same as described in [V.B.3 (V)] except that  $[\text{Pt}(\text{PPh}_3)_4]$  was used in place of  $[\text{Pd}(\text{PPh}_3)_4]$ . The yellow orange compound which was obtained as the reaction product was analysed for  $[\text{Pt}(\text{PPh}_3)_2(\text{NCS})_2]$ .

V.C Analyses and Physico chemical measurements

Carbon, hydrogen and nitrogen in the products were analysed by the Microanalytical Laboratory of the Indian Institute of Technology, Kanpur, India. The percentage of sulphur and halide in the

samples were estimated by the methods described elsewhere [8-9]. I.R. spectra in KBr discs, m.p. and magnetic susceptibilities at room temperature of the complexes were recorded on a Perkin Elmer 580 spectrophotometer, Fisher Johns melting point apparatus and Guoy balance respectively.

Microanalytical and other physical data of the complexes are given in table V.1.

#### V.D Results and discussion

The results of the reactions of the metal ions and their complexes with NTU in presence of different coligands are shown in Table (V.1). These indicate that in most cases the reactions yield their thiocyanates in reasonably good yields (ca. 60 ). Since some of the products are literature known, they have been identified by their elemental analyses and by comparing their colours, melting points, mixed melting points, i.r. spectra and magnetic susceptibility data with those of the authentic samples.

Reactions of NTU with metal ions and complexes in presence of coligands were carried out strictly under the conditions used in the literature for the metal nitrosyl synthesis. The reactions of NTU with the salts of Mn(II), Fe(II), Ni(II), Ag(I), Cd(II) and Hg(II) [10-17] ions in presence of pyridine and those of Co(II), Ni(II) and Cu(II) ions in presence of 2,2'-bipyridyl and 1,10-phenanthroline [18],  $[\text{Pd}(\text{PPh}_3)_4]$  and  $[\text{Pt}(\text{PPh}_3)_4]$  [19] yielded the literature known thiocyanato complexes. While Co(II), Cr(II)

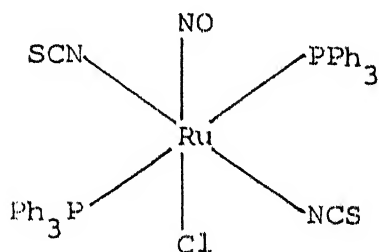
and Zn(II) under the similar reaction conditions yielded different complexes. Cr(II) acetate in presence of pyridine yielded a white complex which was analysed for  $[\text{Cr}(\text{NCS})_3(\text{py})_2 \cdot \text{H}_2\text{O}]$ . Its i.r. spectrum displayed an intense split band around  $1965 \text{ cm}^{-1}$  ( $\nu_{\text{CN}}$ ), a weak to medium intense band, around  $760 \text{ cm}^{-1}$  ( $\nu_{\text{CS}}$ ) and medium intense band around  $450 \text{ cm}^{-1}$  ( $\delta_{\text{NCS}}$ ) besides the characteristics bands of pyridine. The positions of these bands have been interpreted as resulting from the linkage of ambidentate ligand, NCS, through N atom [20]. The salts of Zn(II) and Co(II) yielded complexes having empirical formula  $[\text{Zn}(\text{py})_3(\text{NCS})_2] \cdot \text{H}_2\text{O}$  and  $[\text{Co}(\text{py})_3(\text{NCS})_2]$  or  $[\text{Co}(\text{py})_6][\text{Co}(\text{NCS})_4]$  respectively. The solution of cobalt complex in ethanol is deep blue from which pink needle shaped crystals having cobalt in the anion separated on slow evaporation. If the solution of the latter pink crystals were passed through a column of cation exchanger in ethanol or methanol, the elute on treatment with tetramethyl, tetraethyl or tetrabutyl ammonium chloride yielded  $[(\text{CH}_3)_4\text{N}]_2[\text{CoCl}_2(\text{SCN})_2]$ ,  $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{CoCl}_2(\text{SCN})_2]$  and  $[(\text{C}_4\text{H}_9)_4\text{N}]_2[\text{Co}(\text{SCN})_4]$  respectively.

Although the formation of thiocyanato complexes by nearly all the metal ions suggest the generality of the reaction course, of interest here are the reactions of ruthenium and rhodium ions and their complexes which also pick up NO, along with SCN ions. Considering the remarkable affinities of these metal ions for NO ligands [21], the products obtained by the reactions of these metal ions were not unexpected.  $[\text{Ru}(\text{NO})(\text{NCS})_2\text{Cl}(\text{PPh}_3)_2]$  is the first

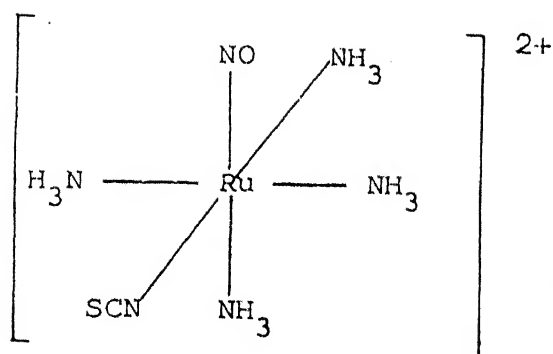
nitrosyl derivative of ruthenium of this type, though other mixed halide derivatives of ruthenium have already been reported.

Bright yellow orange crystalline diamagnetic Ru(II) complex  $[\text{Ru}(\text{NO})(\text{NCS})_2\text{Cl}(\text{PPh}_3)_2] \cdot 1/2 \text{CH}_2\text{Cl}_2$  obtained by the reaction of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  with NTU exhibited in its i.r. spectrum an intense band at  $1875 \text{ cm}^{-1}$  ( $\nu_{\text{NO}^+}$ ) besides the characteristic bands of  $\text{PPh}_3$  and another band at  $2080 \text{ cm}^{-1}$  corresponding to  $\nu_{\text{CN}}$ . Other characteristic bands of NCS group are also present in the region of  $860 \text{ cm}^{-1}$  and  $470 \text{ cm}^{-1}$  assigned to ( $\nu_{\text{C=S}}$ ) and ( $\delta_{\text{NCS}}$ ) respectively. Since for M-NCS bonding,  $\nu_{\text{CN}}$  and  $\nu_{\text{CS}}$  fall approximately in the ranges ( $2080\text{--}2040 \text{ cm}^{-1}$ ), ( $860\text{--}780 \text{ cm}^{-1}$ ) and ( $450\text{--}470 \text{ cm}^{-1}$ ), it is presumed that the NCS group in the complex is bonded through N, atom. Furthermore it is well known that the nitrosyl group ( $\text{NO}^+$ ) is strongly trans directing [22] and prefers to coordinate trans to the ligand of weakest trans influence in a given complex. Since the trans influence of chloride ions is less than that of thiocyanate [22] we suggest that NO group is bonded to the metal ion trans to the chloride ions and equilibrium between  $[\text{Ru}(\text{NO})(\text{NCS})_3-(\text{PPh}_3)_2]$  and  $[\text{Ru}(\text{NO})\text{Cl}(\text{NCS})_2(\text{PPh}_3)_2]$  will favour the latter complex. In addition, since NCS ions in the system are present in very large excess compared to  $\text{Cl}^-$  ions, it is expected that dichloro derivative  $[\text{Ru}(\text{NO})\text{Cl}_2(\text{NCS})(\text{PPh}_3)_2]$  should be less preferred over the dithiocyanato complex. Evidence for the trans positions of  $\text{PPh}_3$  groups comes from the fact that ( $\nu_{\text{CN}}$ ),  $\nu_{\text{CS}}$  bands appear as single bands suggesting (1) the position of NCS groups trans to each other and

(2) in the complex  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$  both the phosphine molecules prefer to bind metal ion in the trans position rather than in the cis [23].



The reaction of  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  with NTU in aqueous medium led to a yellow nitrosyl containing product of stoichiometry  $[\text{Ru}(\text{NO})(\text{NCS})(\text{NH}_3)_4]\text{Cl}_2$ . In view of the (1) elemental analyses which indicated the empirical formula  $[\text{Ru}(\text{NO})(\text{NCS})(\text{NH}_3)_4]\text{Cl}_2$  (2) infra red spectrum which indicated the presence of  $\text{NO}^+$  ( $\nu_{\text{NO}^+}$   $1875\text{ cm}^{-1}$ ),  $\text{NCS}^-$  group ( $\nu_{\text{CN}}$ ,  $2080\text{ cm}^{-1}$  (strong sharp)),  $\nu_{\text{CS}}$ ,  $860\text{ cm}^{-1}$  (weak);  $480\text{ cm}^{-1}$   $\delta_{\text{NCS}}$  (medium intensity)) besides the characteristic bands of  $\text{NH}_3$ , (3) ion exchange studies indicating the presence of NCS group inside the coordination sphere (anion exchanger exchanges all the  $\text{Cl}^-$  ions and not the NCS group and cation exchanger retains the NCS group and  $\text{Cl}^-$  ions are eluted out) and (4) NO being strong trans directing, prefers to coordinate  $\text{NH}_3$  molecule (weak trans directing group) in its trans position, the following structure is proposed. However other structures may also be possible.



The nitrosyl containing species of rhodium  $[\text{Rh}(\text{NO})(\text{NCS})\text{Cl}(\text{PPh}_3)]$  was synthesized by the reaction of NTU with  $[\text{RhCl}(\text{PPh}_3)_3]$ . The reaction proceeds with the oxidation of Rh from +1 to +3. The only species present in the system which may possibly act as an oxidising agent is  $\text{NO}^+$  which might have been picked up by the Rh(I) during the intramolecular trans migration of  $\text{NO}^+$  from sulphur to nitrogen (cf. Scheme 1). Since Rh(III) prefers octahedral structure in its complexes, four coordination around Rh(III) in the complex is highly unexpected. However, of pertinent here is the position of  $\nu_{\text{CN}}$  band ( $2110 \text{ cm}^{-1}$ ) that appeared at a relatively higher position in its i.r. spectrum which points to the bridging nature of the NCS group. Furthermore  $\nu_{\text{CS}}$  and  $\delta_{\text{NCS}}$  also span the range of the bridging nature of the NCS group. It is unfortunate that we are not in a position to confirm the Rh-Cl band because of the presence of a large number of ligand bands in that region. The presence of a band at  $1630 \text{ cm}^{-1}$  in its i.r. spectrum besides the characteristic bands of  $\text{PPh}_3$  suggested coordinated  $\text{NO}^-$  group. In view of these results, tentatively an octahedral structure of the rhodium complex with bridging  $\text{NCS}^-$  and  $\text{Cl}^-$  ions besides the  $\text{NO}^-$  and  $\text{PPh}_3$  molecules bonded trans to each other have been proposed. Another possibility

of  $\text{NO}^-$  and bridging  $\text{Cl}^-$  coordinated in trans position also exists. It is however not possible to decide in between the many alternating structures of this complex.

The reaction of iridium complex with NTU yielded an octahedral complex  $[\text{Ir}(\text{PPh}_3)_2(\text{NCS})_2\text{Cl}(\text{Thiourea})]$ . To confirm the coordination of thiourea, the complex has been recrystallized a number of times in different solvents and allowed to pass through the sephadex-10 column. In every case the eluted complex was identical with the starting material. The i.r. spectrum of the product exhibited the bands given in the Table V.1, which suggested S-bonded thiocyanate which is not unexpected because of 'b' character of iridium. In addition, all the characteristic bands of  $\text{PPh}_3$  and thiourea are also present in the spectrum.

In the remaining products it is note-worthy to observe that NO, group is not linked with metal ions.

Another point of interest is that in all the reaction products despite the fact whether NO is linked with the metal ion or not, thiocyanato group is invariably bonded to the metal ion. This is understandable in the case of Pt and Pd complexes which have more tendency to form complexes in zero valent state rather than the nitrosyl complexes [24]. Besides, in +2 oxidation states they prefer to form  $(\text{N}_2\text{O}_2)^{2-}$  complexes [25] which we assume to be relatively unstable with respect to those of their thiocyanates and, particularly, when NCS concentration is very high in the medium. The same argument may be quoted for first row transition metal ions.

In most cases nitrosyl group is introduced in the complexes of first transition series elements under special reaction conditions. We, therefore, presume that one of the many reasons for NO group not linking with the metal ions of the first transition series may be their greater affinity for NCS group compared to NO, which yield stable S or N bonded thiocyanato complexes depending upon their 'a' or 'b' character.

Emerging conclusion from the foregoing discussion and experimental results is that NTU does not have favourable potentiality for nitrosylation unless the metal ion itself has relatively higher affinity for NO group. The reason which may be put forward for this could be that the reaction (2) is so fast that before picking up  $\text{NO}^+$  by the metal ion for nitrosylation, it migrates to the N atom of thiourea which subsequently decomposed to  $\text{NCS}^-$  by destroying the  $\text{NO}^+$  group and due to higher concentration of NCS, the latter preferentially attacks the metal ions to give thiocyanato complexes rather than nitrosyls.

Reaction carried out, reactants, products, colour, melting point analyses and major ir bands

Reactants	Product	Colour	M.P.	Analyses (Found, Calculated)							Major I.R. bands			
				C	H	N	S	X(Cl)	CN	CS	NCS	N		
2	3	4	5	6	7	8	9	10	11	12	13	14		
I) Acetate+NTU+PY	$[\text{Cr}(\text{NCS})_3(\text{Py})_2] \cdot \text{H}_2\text{O}$	White	260°	38.5 (38.8)	3.17 (2.98)	16.66 (17.4)	23.1 (23.8)	-	2060	760	468			
I) Chloride+PY+NTU	$[\text{Mn}(\text{Py})_4(\text{NCS})_2] \cdot 1/2\text{MeOH}$	-do-	-	52.2 (53.6)	3.6 (4.3)	15.0 (16.6)	12.4 (12.72)	-	2066	798	480			
I) Acetate+PY+NTU	$[\text{Co}(\text{Py})_3(\text{NCS})_2]$	Pink	190°C	51.5 (49.6)	3.64 (3.64)	16.8 (17.03)	16.2 (15.5)	-	2090	760	468			
I) Sulfate+PY+NTU	$[\text{Fe}(\text{Py})_4(\text{NCS})_2]$	Dark Brown (needles)	-	54.5 (54.1)	4.8 (4.09)	17.5 (17.2)	12.94 (13.1)	-	2068	804	470			
(Py) <sub>3</sub> (NCS) <sub>2</sub> +TMAC	$[\text{Co}(\text{NCS})_2\text{Cl}_2][(\text{CH}_3)_4\text{N}]_2$	Blue	-	29.7 (30.5)	5.9 (6.10)	15.0 (14.24)	16.5 (16.28)	-	2090	760	468			
(Py) <sub>3</sub> (NCS) <sub>2</sub> +TEAC	$[\text{Co}(\text{NCS})_2\text{Cl}_2][(\text{C}_2\text{H}_5)_4\text{N}]_2$	Blue	-	32.5 (31.9)	4.8 (5.24)	14.3 (14.6)	16.0 (16.7)	17.5, 2090 (18.6)	2090	760	468			
(Py) <sub>3</sub> (NCS) <sub>2</sub> +TBAC	$[\text{Co}(\text{NCS})_4][(\text{C}_4\text{H}_9)_4\text{N}]_2$	Blue	-	54.9 (55.9)	5.2 (4.14)	10.5 (10.88)	17.2 (16.6)	-	2090	750	470			
II) Acetate/Sulfate ipy + NTU	$[\text{Co}(\text{bipy})_2(\text{NCS})_2]$	Violet Pink	-	52.8 (53.7)	2.75 (3.25)	16.4 (17.1)	12.4 (13.0)	-	2080	762	470			
II) Acetate or Sulfate phen + NTU	$[\text{Co}(\text{phen})_2(\text{NCS})_2]$	Violet Pink	-	57.2 (58.2)	3.27 (3.7)	14.22 (15.7)	10.6 (11.8)	-	1066 2079	762	470			
II) Nitrate+PY+NTU	$[\text{Ni}(\text{Py})_4(\text{NCS})_2]$	Light Blue	-	54.18 (53.7)	4.42 (4.07)	17.4 (17.1)	12.8 (13.03)	-	2079	800	468			
II) Nitrate+Bipy+NTU	$[\text{Ni}(\text{bipy})_2(\text{NCS})_2]$	Green	-	52.8 (53.7)	4.2 (4.07)	17.5 (17.1)	12.3 (13.06)	-	2080 2092	760	465			

...contd.

ntd.)

2	3	4	5	6	7	8	9	10	11	12	13	14
) Nitrate+Phen+NTU	[Ni(phen) <sub>2</sub> (NCS)]	Green	-	53.42 (3.1)	3.5 (3.1)	15.2 (15.7)	11.6 (11.9)	-	2080 2095	762	465	
) SO <sub>4</sub> +Py+NTU	[Cu(py) <sub>2</sub> (NCS) <sub>2</sub> ]	Green	-	42.6 (41.7)	3.95 (4.9)	13.5 (13.93)	16.3 (15.9)	-	2065	770	405	
) Sulfate+Bipy+NTU	[Cu(bipy) <sub>2</sub> (NCS) <sub>2</sub> ]	Pale green	190 dec	52.4 (53.3)	4.5 (4.04)	15.7 (16.96)	11.8 (12.92)	-	2070 2083	765	462	
I) Sulfate+Phen+NTU	[Cu(phen) <sub>2</sub> (NCS) <sub>2</sub> ]	Dark green	does not melt	57 (57.8)	2.98 (3.7)	14.2 (15.58)	10.5 (11.87)	-	2070	780	464	
I) Chloride+Py+NTU	[Zn(py) <sub>3</sub> (NCS) <sub>2</sub> ].H <sub>2</sub> O	White	-	45.56 (46.6)	3.73 (3.89)	16.44 (16.05)	14.8 (14.7)	-	2100 2075	847	485	
1 <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> ]+NTU	[Ru(NO)(NCS) <sub>2</sub> Cl- (PPh <sub>3</sub> ) <sub>2</sub> ][1/2CH <sub>2</sub> Cl <sub>2</sub> ]	Yellow orange	-	54.19 (54.4)	4.48 (3.7)	4.8 (4.9)	7.8 (7.6)	9.1 8.4	2085	855	470	1875
NH <sub>3</sub> ) <sub>5</sub> Cl]+NTU	[Ru(NO)(NH <sub>3</sub> ) <sub>4</sub> NCS]Cl <sub>2</sub>	Orange yellow	-	5.96 (3.59)	7.1 (3.65)	25.23 (25.1)	18.8 (19.16)	18.1 21.2	2080	860	470	1875
1:1(PPh <sub>3</sub> ) <sub>3</sub> ]+NTU	[Rh(NO)NCSCl(PPh <sub>3</sub> )]	Orange	-	46.54 (46.5)	4.18 (3.08)	5.92 (7.3)	6.9 (7.3)	9.01 (6.5)	2120	730		1635
3+Py+NTU	[Ag(py) <sub>2</sub> (NCS) <sub>2</sub> ]	White	-	37.2 (37.7)	2.4 (2.62)	15.8 (14.6)	15.8 (16.8)	-	2090	755	430	
3+Py+NTU	Cd(py) <sub>2</sub> (NCS) <sub>2</sub>	White	190°C	38.92 (37.5)	2.87 (2.6)	13.0 (14.5)	15.2 (16.5)	-	2090	770	469	
1 <sub>3</sub> (PPh <sub>3</sub> ) <sub>3</sub> +NTU	[Ir(PPh <sub>3</sub> ) <sub>2</sub> (NCS) <sub>2</sub> Cl- (thio)]	Orange yellow	260°	48.9 (48.8)	3.4 (6.5)	11.54 (6)	12.1 (10.8)	4.1	2120	765	470	
PPh <sub>3</sub> ) <sub>4</sub> +NTU	[Pd(NCS) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	Yellow orange	-	60.5 (61.07)	3.9 (4.05)	3.7 (3.75)	8.2 (8.5)	-	2100	860	-	
PPh <sub>3</sub> ) <sub>4</sub> +NTU	[Pt(NCS) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	Yellow orange	-	54.6 (53.16)	3.83 (3.66)	3.35 (3.27)	8.5 (9.8)	-	2090	860	-	
II) Chloride+Py+NTU	[Hg(py) <sub>2</sub> (NCS) <sub>2</sub> ]	White	80°C	30.0 (30.4)	2.53 (2.1)	11.89 (11.9)	12.8 (13.5)	-	2130 2025	780	460	

pyridine, bipy: 2,2'-bipyridyl, phen: 1,10-phenanthroline, TMAC: tetramethyammonium chloride, TEAC: tetraethyl ammonium chloride,

LEGEND TO THE FIGURES

Fig. V.1 (A)  $[\text{Cr}(\text{NCS})_3(\text{py})_2]$

(B)  $[\text{Zn}(\text{py})_3(\text{NCS})_2]$

Fig. V.2 (A)  $[\text{Co}(\text{bipy})_2(\text{NCS})_2]$

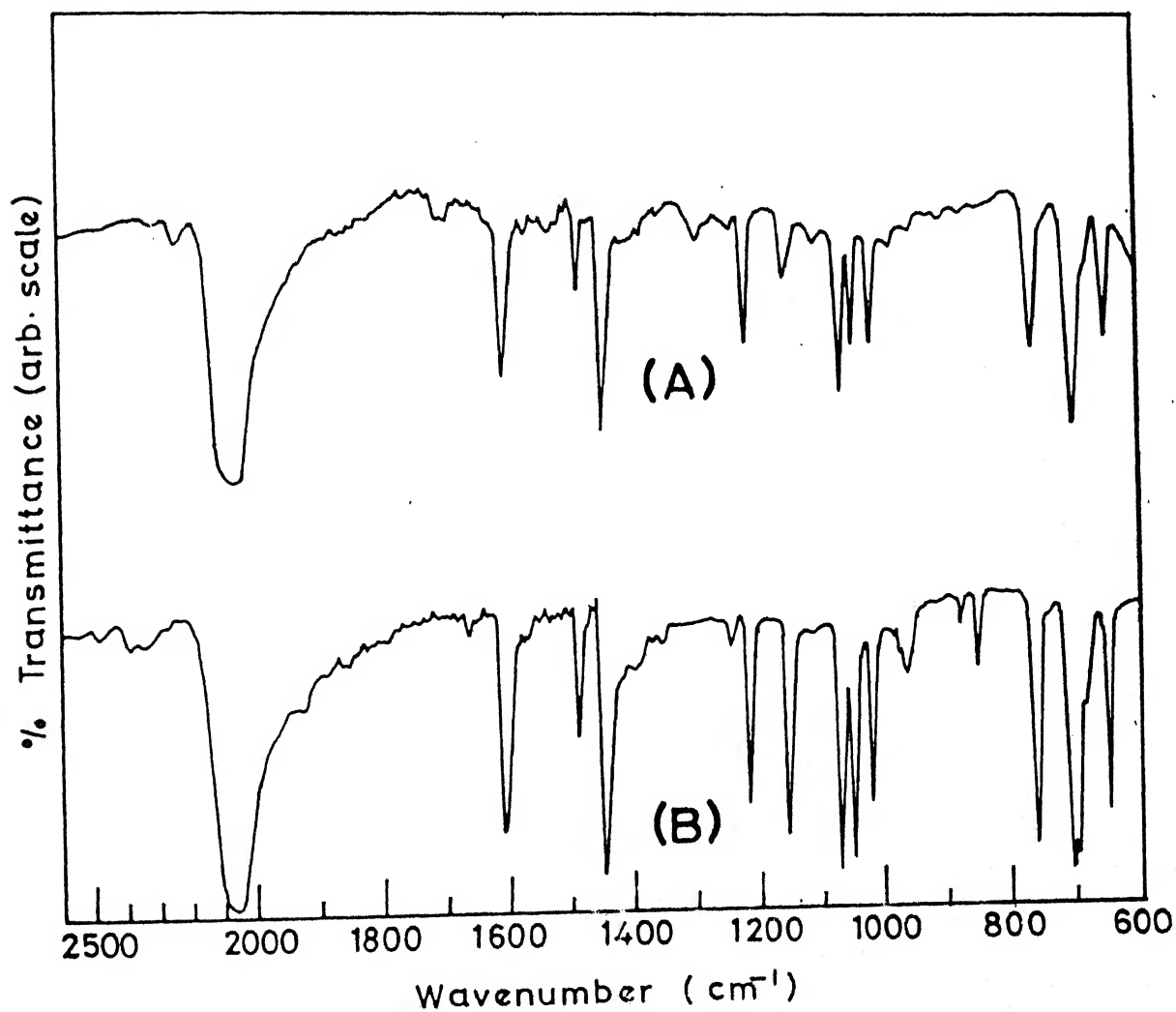
(B)  $[\text{Co}(\text{phen})_2(\text{NCS})_2]$

Fig. V.3 (A)  $[\text{Ru}(\text{NO})(\text{NCS})_2\text{Cl}(\text{PPh}_3)_2]$

(B)  $[\text{Ru}(\text{NO})(\text{NCS})(\text{NH}_3)_4]\text{Cl}_2$

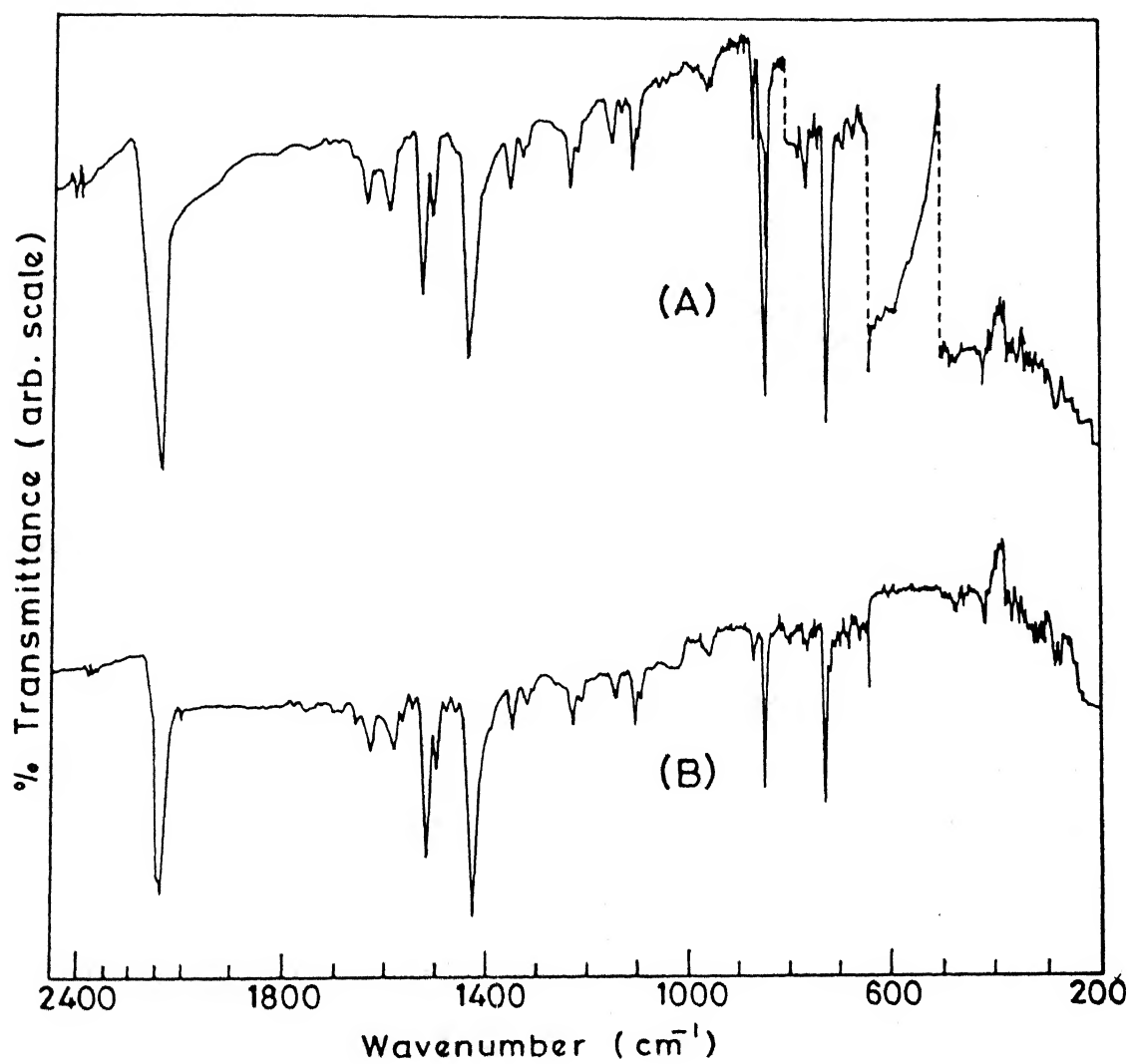
Fig. V.4 (A)  $[\text{Rh}(\text{NO})\text{NCSCl}(\text{PPh}_3)]$

(B)  $[\text{Ir}(\text{NCS})_2(\text{PPh}_3)_2\text{Cl}(\text{thiourea})]$



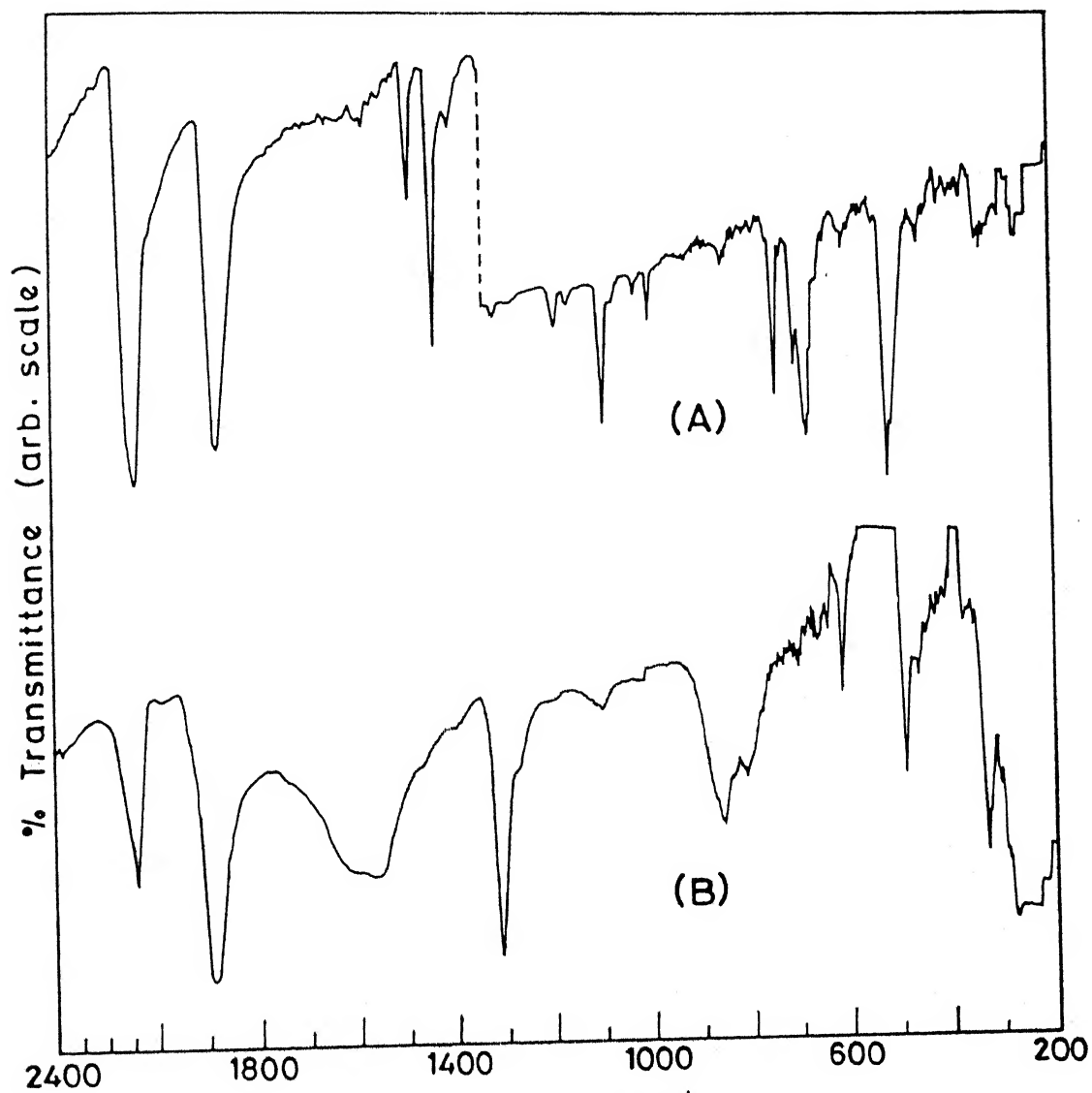
Infrared spectra

FIG.V.1



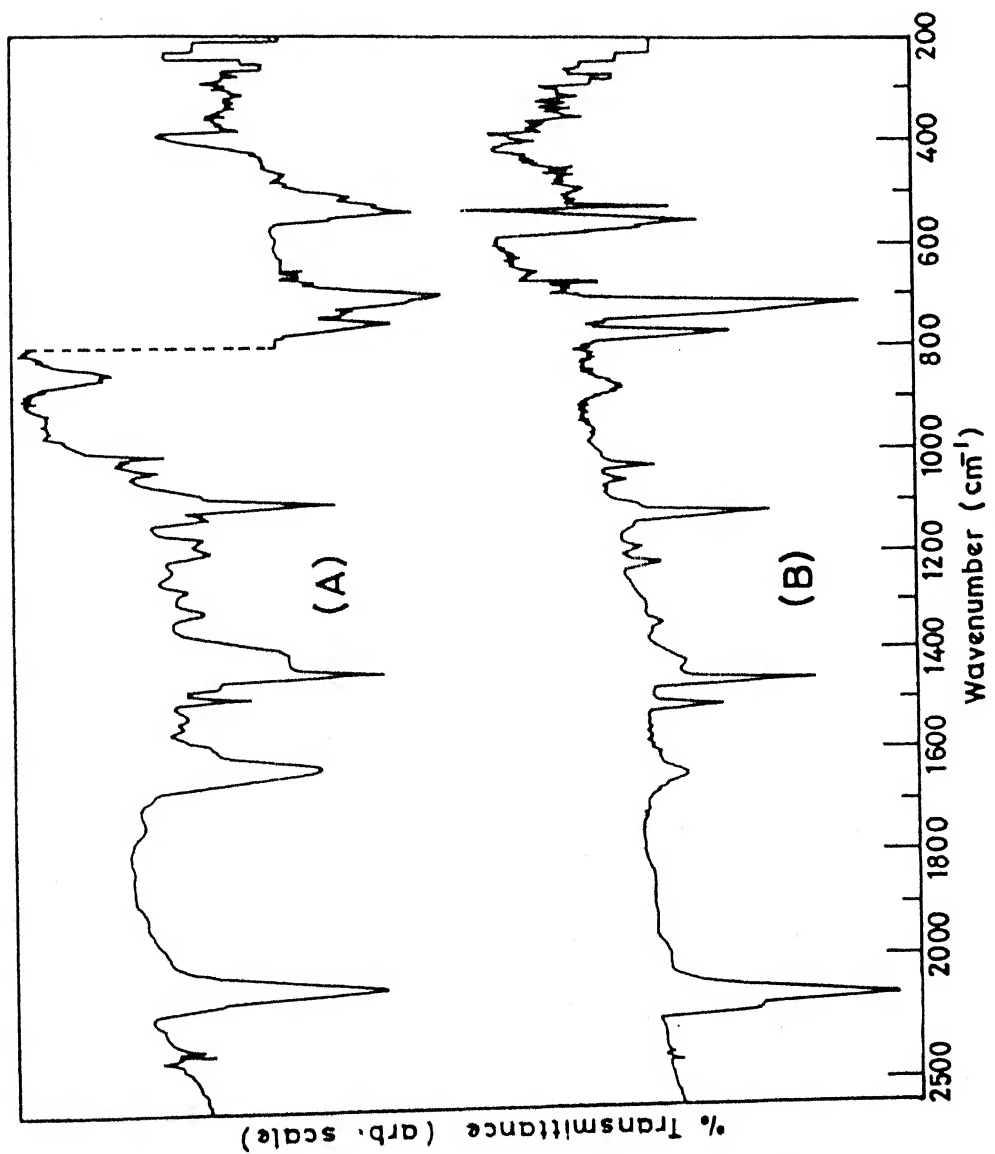
Infrared spectra

FIG.V.2



Infrared spectra

FIG. V. 3



Infrared spectra  
FIG. V.4

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## CHAPTER SIX

### ALKYL NITRITES AS NITROSYLATING AGENTS

Although a number of syntheses of metal nitrosyls are available in literature, the interaction of gaseous NO with metal ions and their complexes still remains the method of choice. On the other hand thermodynamic instability coupled with its being menacing pollutant sometimes puts a constraint on the use of NO as a nitrosylating agent. One possible route where direct use of NO is avoided could be in situ generation of NO through the cleavage of weak O-NO bond, with subsequent trapping by the metal ions. Literature survey indicates practically no work in this direction except the use of pentyl and isopentyl nitrites [1,2] as the nitrosylating agents in a couple of reactions only. A detailed study of reaction of various alkyl nitrites may therefore assist in their utility for the synthesis of metal nitrosyls. The present chapter describes the synthesis of known metal nitrosyls using alkyl nitrites (methyl, ethyl, propyl and n-butyl) as nitrosylating agents for the first ti

## VI.A Materials and Methods

The reactions and operations described below were carried out under oxygen-free nitrogen atmosphere. All the solvents were thoroughly degassed before use. Solvents and reagents were purified by standard methods. Alkyl nitrites (methyl [ 3 ], ethyl [ 4 ], propyl [ 5 ] and butyl [ 6 ]) and  $[\text{Fe}(\text{Py})_4\text{Cl}_2]$  [ 7 ] were prepared by the literature procedures. The ligands maleonitrile dithiolate [ 8 ], 5,7-dinitroaminoquinoline, acetylacetone-ethylenediamine and benzoyl-acetone-ethylenediamine [ 9 ] were prepared by the literature methods.

## VI.B Synthetic Procedures

Following are the typical procedures for the interaction of alkyl nitrites with the metal ions and their complexes.

### (I) Reaction of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with methyl/ethyl nitrite in presence of maleonitrile dithiolate and bipyridyl

Methyl/ethyl nitrite gas was passed for 30-40 min. through a deaerated methanolic solution (25 ml) of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (15 mmol). Methanolic solution (20 ml) of maleonitrile dithiolate (5 mmol) was added to this solution with vigorous stirring followed by bipyridyl (5 mmol) in dichloromethane (25 ml) and the resulting solution stirred for 2-3 hr at room temperature whereupon dark brown crystals separated out. These were filtered, washed with ethanol, ether and dried in vacuo.

(II) Reaction of  $[\text{Fe}(\text{Py})_4\text{Cl}_2]$  with methyl/ethyl nitrite in presence of bipyridyl and maleonitrile dithiolate

Methyl/ethyl nitrite gas was passed for 45 min through a solution (25 ml) of  $[\text{Fe}(\text{Py})_4\text{Cl}_2]$  in  $\text{CH}_2\text{Cl}_2$ :MeOH (1:1) and to the resulting mixture were added methanolic solution (25 ml) of maleonitrile dithiolate and a  $\text{CH}_2\text{Cl}_2$  solution (25 ml) of bipyridyl in succession. The resulting mixed solution was stirred for about 2-3 hr when a brown microcrystalline compound separated out. It was filtered, washed with ethanol, ether and dried in vacuo.

(III) Reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with methyl/ethyl/propyl/n-butyl nitrite in presence of  $\text{LiClO}_4$  and bipyridyl

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.25g) and  $\text{LiClO}_4$  (0.2g) were dissolved in absolute ethyl alcohol (25 ml) and the solution was deaerated by flushing with nitrogen gas. To this solution methyl/ethyl nitrite gas was passed for 1.5 hr [in case of butyl and propyl nitrites, 10 ml of the nitrite were added to the solution]. To the resulting solution bipyridyl (0.37g) in hot ethanol (10 ml) was added and stirred for 30 min at room temperature whereupon a microcrystalline compound analysing for  $[\text{Co}(\text{dipy})_2(\text{NO})\text{Cl}]\text{ClO}_4$  separated out. It was filtered, washed with ethanol, ether and dried in vacuo.

- (IV) Reaction of  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  with methyl/ethyl/propyl/n-butyl nitrite in presence of dimethylglyoxime

$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (2.5 mmol) was dissolved in methanol (25 ml) and the solution cooled to  $0^\circ\text{C}$ . Methyl/ethyl nitrite gas (10 ml solution of butyl/propyl nitrite) was passed through it for 2 hr. To this was added a solution of dimethylglyoxime (0.23 mmol) in methanol (15 ml) dropwise with continuous stirring whereupon a black compound, analysing for  $[\text{Co}(\text{dmgh})_2\text{NO}]$  separated out, which was filtered, washed with water, ethanol and dried in vacuo.

- (V) Reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with methyl/ethyl nitrite in presence of triphenylphosphine and triethylamine

A solution of triethylamine, triphenylphosphine and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in 1:2:1 molar ratio in methanol (50 ml) was purged with  $\text{N}_2$  gas and through this solution was passed ethyl/methyl nitrite gas for 30-45 min. A brown solid, analysing for  $[\text{Co}(\text{NO})(\text{PPh}_3)_2\text{Cl}_2]$  separated out, which was filtered, washed with ethanol, ether and dried in vacuo.

- (VI) Reaction of chromous acetate with methyl/ethyl nitrite in presence of diethyl dithiocarbamate

The procedure used was similar to that of Malatesta [10]. To a saturated solution of diethyl dithiocarbamate (250 mg) in ethanol (25 ml) a cold saturated solution of chromous acetate was added. Methyl/ethyl nitrite gas was passed through this solution

continuously for 2.5 hr, filtered and the filtrate evaporated to dryness under reduced pressure. The residue was extracted with benzene and the benzene extract evaporated to dryness under reduced pressure to afford a deep red oil. It was placed in an evacuated desiccator. When the volume of this solution was reduced to half, some crystals of  $[\text{Cr}(\text{NO})_2 \text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2 \text{ 2}]$  separated out, which were filtered, and dried in vacuo, m.p. 105.

(VII) Reaction of Co(II) acetylacetonate with alkyl nitrites

A solution of Co(II) acetylacetonate (0.5g) in dichloromethane-methanol (50 ml, 1:1) was degassed by flushing with nitrogen gas at 15°C. Ethyl/methyl nitrite gas (or 10 ml of n-butyl nitrite) was passed through the solution for 30 min and the resulting solution concentrated to about 10 ml. On the addition of petroleum ether to the concentrated solution crystals of  $[\text{Co}(\text{acac})_2\text{NO}]$  separated out, which were filtered, washed with ethanol and dried in vacuo.

(VIII) Reaction of Co(II) acetylacetonatoethylenediamine with methyl/ethyl nitrite gas

Co(II) acetylacetonatoethylenediamine (1 mmol) was dissolved in dichloromethane-ethanol (25 ml, 1:1) and the solution cooled to 0°C. Ethyl/methyl nitrite gas was bubbled through the cooled solution for 30 min at 0°C. The colour of the solution changed from reddish yellow to brown. On the addition of petroleum ether to the resulting solution, a black brown crystalline compound

precipitated out, which was filtered and dried in vacuo.

(IX) Reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with methyl/ethyl nitrite in presence of ammonia solution

The reaction was carried out according to the method of Mellor and Kraig [14].  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.5g) was dissolved in water (20 ml), the solution treated with ice cooled ammonia solution (10 ml) and degassed by flushing with nitrogen gas with intensive cooling. Ethyl/methyl nitrite gas was passed through the solution for 1-2 hr whereby black crystals of  $[\text{Co}(\text{NH}_3)_5\text{NO}]_2\text{Cl}_4$  separated out. These were filtered, washed with water, ethanol and dried in vacuo.

VI.C Analyses and Physicochemical Measurements

Carbon, hydrogen and nitrogen analyses were performed in the Microanalytical Laboratory of the Indian Institute of Technology, Kanpur, India. Halide and sulfur contents in the samples were determined by the method described elsewhere [12,13]. Infrared spectra of the compounds were recorded in KBr on a Perkin-Elmer 580 spectrophotometer. Melting points and magnetic susceptibilities at room temperature, of the complexes were recorded on a Fisher John melting point apparatus and Guoy balance respectively.

Microanalytical and other physical data of the complexes are given in Table VI.1.

#### VI.D Results and Discussion

The nitrosyl complexes of cobalt, iron and chromium were synthesized by passing methyl or ethyl nitrite gas through solution of their complexes and salts. In a few cases the higher alkyl nitrites like propyl and butyl could also be used with almost similar results. The nitrosylating agents were, therefore, confined to the methyl or ethyl nitrite in all the experiments. After purification by recrystallization the complexes were characterized by a number of physicochemical techniques. Elemental analyses of the complexes and the position of  $\nu_{\text{NO}}$  in their IR spectra are summarized in Table I. In order to further confirm the identity of the complexes these were also synthesized by the literature methods using NO gas as nitrosylating agent and the properties of the products thus obtained were identical with these obtained presently. It has, therefore, been felt that the alkyl nitrites especially methyl and ethyl nitrites can be successively used as nitrosylating agents and that too under ambient conditions.

We, further surmise that in these nitrosylating reactions possibly in alcoholic medium alkyl nitrites get hydrolysed [14] with the subsequent generation of NO or  $\text{HNO}_2$  which is picked up by the metal salts or their complexes to give the respective metal nitrosyl. Our experiments (unpublished work) also indicate that these nitrite can be successfully used in the nitrosylation of II and III transition metal series also.

Table VI.1. Characterisation Data of Various Nitrosyls Synthesised

Sl. No.	Compound	$\nu_{\text{NO}}$ $\text{cm}^{-1}$	Found(calc) /					X(=Cl,Br)	Proce- dure	Reactants used
			C	H	N	S				
1	2	3	4	5	6	7	8	9	10	
1.	[Co(mnt)(bipy)NO]	1670	37.3 (37.0)	2.0 (1.9)	13.1 (13.3)	16.6 (18.3)	-	I	CoCl <sub>2</sub> .6H <sub>2</sub> O+mnt+bip	
2.	[Co(mnt)(phen)NO]	1670	47.1 (47.4)	2.0 (2.2)	17.2 (17.0)	15.6 (15.3)	-	I	CoCl <sub>2</sub> .6H <sub>2</sub> O+mnt+phe	
3.	[Co(mnt)(PFPh <sub>3</sub> ) <sub>2</sub> NO]	1805 1850	63.8 (63.3)	4.0 (4.3)	5.5 (5.9)	5.4 (8.4)	-	I	CoCl <sub>2</sub> .6H <sub>2</sub> O+mnt+PFPh	
4.	[Co(ach)(mnt)NO]	1620	30.2 (29.8)	2.8 (2.4)	15.6 (15.9)	17.9 (18.0)	-	I	Co(II)acetate+ach +mnt	
5.	[Co(ach) <sub>2</sub> NO](NO <sub>3</sub> ) <sub>2</sub>	1680	50.8 (50.5)	5.2 (5.4)	22.2 (22.4)	-	-	I	Co(II)nitrate+ach	
6.	[Fe(mnt) <sub>2</sub> NO][Fe(bipy) <sub>2</sub> NO]	1620	37.4 (37.2)	2.1 (2.3)	16.5 (16.9)	16.6 (16.2)	-	II	Fe(py) <sub>4</sub> Cl <sub>2</sub> +mnt+bip	
7.	[Fe(mnt) <sub>2</sub> NO][Fe(phen) <sub>2</sub> NO]	1625 1820	47.2 (47.4)	2.0 (1.7)	15.5 (15.1)	15.7 (14.9)	-	II	Fe(py) <sub>4</sub> Cl <sub>2</sub> +mnt+phe	
8.	[Co(bipy) <sub>2</sub> (NO)Cl]ClO <sub>4</sub>	1642	44.9 (45.1)	3.00 (2.95)	13.0 (12.5)	-	12.0 (13.0)	III	CoCl <sub>2</sub> +bipy+LiClO <sub>4</sub>	
9.	[Co(bipy) <sub>2</sub> (NO)Cl]PF <sub>6</sub>	1642	41.2 (41.5)	2.8 (3.17)	12.0 (12.2)	-	6.0 (6.3)	III	CoCl <sub>2</sub> +bipy+NH <sub>4</sub> PF <sub>6</sub>	

...contd.

Table VI.1 (contd.)

1	2	3	4	5	6	7	8	9	10
0.	$[\text{Co}(\text{bipy})_2(\text{NO})\text{NO}_2]\text{ClO}_4$	1642	42.7 (41.9)	2.9 (3.4)	14.9 (14.5)	-	6.2 (5.8)	III	$\text{Co}(\text{NO}_3)_2 + \text{bipy} + \text{LiClO}_4$
1.	$[\text{Co}(\text{dmgh})_2\text{NO}]$	1640	30.1 (29.8)	4.4 (4.6)	22.0 (21.5)	-	-	IV	$\text{Co}(\text{II})\text{acetate} + \text{dmg}$
2.	$[\text{Co}(\text{dmgh})_2(\text{NO})\text{H}_2\text{O}]$	1640	27.1 (26.5)	4.9 (4.4)	19.8 (19.7)	-	-	IV	$\text{Co}(\text{II})\text{acetate} + \text{dmg}$
3.	$[\text{Co}(\text{NO})(\text{PPh}_3)_2\text{Cl}_2]$	1638	63.2 (62.8)	4.4 (4.8)	2.1 (1.96)	-	10.6 (10.6)	V	$\text{CoCl}_2 + \text{PPh}_3 + \text{Triethylamine}$
4.	$[\text{Co}(\text{NO})_2(\text{PPh}_3)_2\text{B}(\text{C}_6\text{H}_5)_4]$	-	74.8 (74.3)	5.2 (5.4)	2.9 (2.76)	-	-	V	$\text{CoCl}_2 + \text{PPh}_3 + \text{Triethylamine} + \text{NaBPh}_4$
5.	$[\text{Co}(\text{en})_2\text{NO}](\text{ClO}_4)_2$	1610	11.8 (10.8)	4.0 (4.2)	17.2 (16.8)	-	17.4 (18.3)	IV	$\text{Co}(\text{ClO}_4)_2 + \text{en}$
6.	$[\text{Co}(\text{en})_2\text{NO}](\text{NO}_3)_2$	1645	14.4 (14.6)	4.8 (5.1)	29.4 (28.3)	-	-	IV	$\text{Co}(\text{NO}_3)_2 + \text{en}$
7.	$[\text{Co}(\text{py})_4\text{NO}](\text{ClO}_4)_2$	1660	39.7 (39.8)	3.3 (3.9)	11.6 (11.4)	-	11.6 (12.1)	IV	$\text{Co}(\text{ClO}_4)_2 + \text{Py}$
8.	$[\text{Co}(\text{PPh}_3)_2(\text{NO})_2]\text{ClO}_4$	1800 1850	58.2 (58.1)	4.0 (4.3)	3.8 (3.4)	-	4.8 (5.2)	IV	$\text{Co}(\text{ClO}_4)_2 + \text{PPh}_3$
9.	$[\text{Cr}(\text{NO}_2)\{\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2\}_2]$	1660 1720	20.6 (21.2)	5.7 (4.8)	16.0 (15.8)	37.3 (37.2)	-	V	Chromous acetate + dtc

r.

...contd.

Table VI.1 (contd.)

1	2	3	4	5	6	7	8	9	10
0.	$[\text{Co}(\text{NH}_3)_5\text{NO}](\text{NO}_3)_2$	1610	-	-	-	-	-	IX	
1.	$[\text{Co}(\text{NH}_3)_5\text{NO}][\text{Br}_2\cdot\text{H}_2\text{O}]$	1610	-	-	-	-	-	IX	
2.	$[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$	1610	-	-	-	-	-	IX	
3.	$[\text{Co}(\text{NH}_3)_5\text{NO}]\text{I}_2$	1610	-	-	-	-	-	IX	

mnt = Maleonitrile dithiolate; bipy = bipyridyl; phen = 1,10-phenanthroline; ach = 7-aminoquinoline; TPP = triphenylphosphine; diphos = diphenylphosphinoethane; en = ethylenediamine; Py = pyridine; dmg = dimethylglyoxime; dtc = diethyl dithiocarbamate; acac = acetylacetone; AE = acetylacetone ethylenediamine; BE = benzoylacetoneethylenediamine; salen = salicylaldehydeethylenediamine.

+ MEONO/ETONO passed through the solution for 2-3 hr at 0°C.

† MEONO/ETONO passed through the solution at 0°C for 3 hr.

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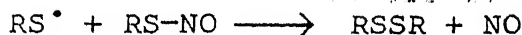
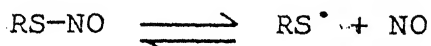
## CHAPTER SEVEN

### RELATIVE EFFICIENCY OF THE THIONITRITES (PT, TTN, S-NITROSOCYSTEINE AND NTU) USED FOR METAL NITROSYLATION

Although a number of synthetic procedures like, interaction of metal ion and their complexes with NOX ( $X = Cl^-$ ,  $Br^-$ ,  $Br_3^-$  and  $NO_2^-$ ), alkyl and alkali nitrites, hydroxylamines, dinitrogen trioxide, concentrated nitric acid, transition metal nitrosyls and N-nitrosamides are available in the literature for nitrosylation, but all except a few have been used for nitrosylation of some specific metal ions or their complexes. NO is the most used nitrosylating agent and one may therefore classify it as a general nitrosylating agent. It, however, has a number of other restraints. In the present study the possible application of organic S-nitrosoderivatives have been examined for the trans nitrosation reactions with the metal ions and their complexes.

Thionitrites undergo both thermal and photolytic decomposition in a homolytic fashion to give nitric oxide and the free radical  $RS^\bullet$ . The latter can either abstract a hydrogen atom from

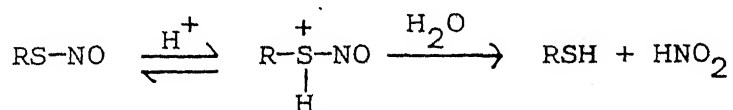
the solvent to yield thiol or form disulfide by reacting with another molecule of thionitrite.



NO thus released, may react with the metal ions and their complexes present in the reaction medium to give the corresponding metal nitrosyls. Depending upon the nature of R in RS, the half lives of their thermal decomposition vary from a few seconds to a few months.

It has been established that a few thionitrites, stable at room or lower temperatures decompose very slowly ( $\text{CF}_3\text{C-SNO}$  decomposes very rapidly at room temperature but very slowly at  $-78^\circ\text{C}$ ) while some are unstable, even at low temperatures. Thus one may utilize the thionitrites which are stable at lower temperatures for the synthesis of those metal nitrosyls that are prepared at high temperature and vice-versa.

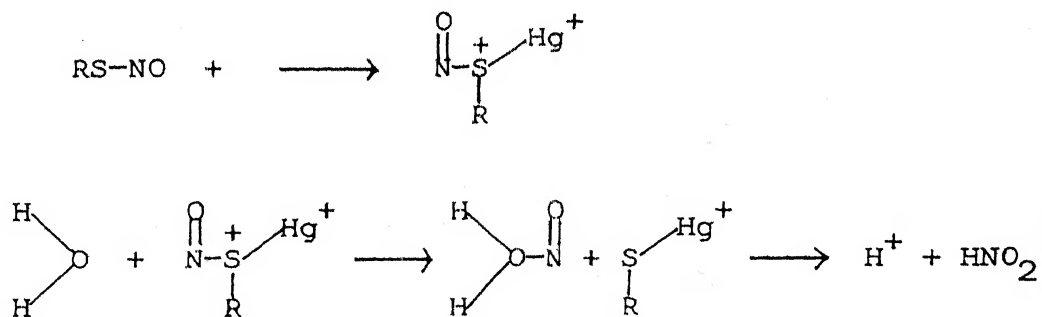
In strongly acidic solution thionitrites denitrosate yielding NO and corresponding thiol



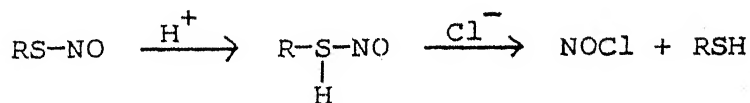
The reaction is reversible with the equilibrium lying well over to the side of thionitrite. It can however proceed towards right in presence of  $\text{HNO}_2$  scavenger. Nitrous acid traps like, sodium

azide, ascorbic acid, aniline derivatives and sulphanic acid have been used for this purpose. It is possible to denitrosate thionitrite in presence of sufficiently high concentration of  $\text{HNO}_2$  scavanger. The metal ions and their complexes having high affinity for  $\text{HNO}_2$  or  $\text{NO}$ , if present in the system, may also act as scavenger by picking the generated  $\text{NO}$  and thus yield metal nitrosyls.

It has also been found that the denitrosation reaction is catalysed by the mercuric salts like  $\text{HgCl}_2$ ,  $\text{HCl}$  gas and  $\text{Cl}^-$  ions in presence of a scavanger.



$\text{HCl}$  gas used in the reaction may be a good source for both  $\text{H}^+$  and  $\text{Cl}^-$  ions and thereby enhancing the rate of denitrosation of thionitrites.



Thus, the presence of  $\text{HCl}$  or  $\text{HgCl}_2$  in the reaction medium enhances the rate of denitrosation of thionitrites and in this way might increase the yields of nitrosylation reactions.

Present work in the thesis has described a convenient single step synthesis of a number of nitrosyl complexes based on the application of S-nitroso derivatives. We have chosen four thionitrites, Penicillamine thionitrite (PT), Tritylthionitrite (TTN), S-nitrosocysteine and nitrosothiourea (NTU) for this purpose. PT and TTN are stable and decompose only at high temperatures, S-nitrosocysteine at room temperature while NTU is stable only at lower temperatures. This short chapter describes the difference in behaviour of these thionitrites towards metal nitrosylation reactions.

Results obtained from the nitrosylation reactions, utilizing penicillamine thionitrite as nitrosylating agent clearly indicated that in almost all the reactions, at elevated temperatures pure nitrosyl complexes were obtained in reasonably good yields ( $\approx 70\%$ ) except in a few cases where hyponitrite complexes were formed. We however, were not able to get any nitrosyl complexes at room or lower temperature using this reagent. This may be due to the fact that penicillamine thionitrite is very stable at room or lower temperatures and dissociation process may be so slow that the concentration of NO present at a particular time in the reaction might not be sufficient enough to nitrosylate metal ions or their complexes. Changing the reaction conditions except temperatures did not make any difference in its nitrosylation properties. The observations favour the general applicability of penicillamine thionitrite at higher temperature. Furthermore, its thiols, thio

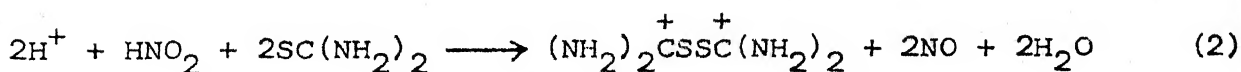
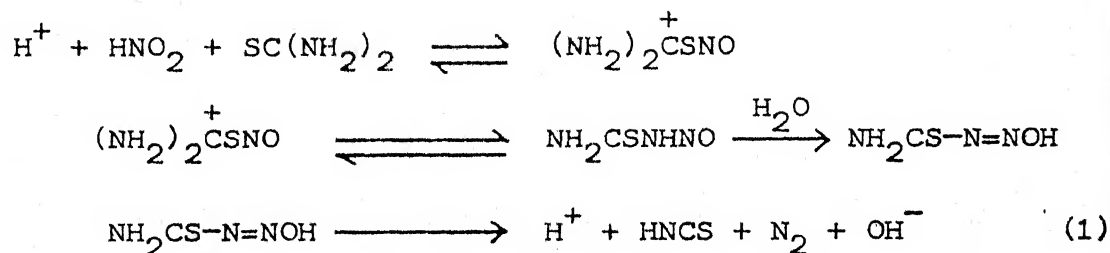
radical or disulfide did not coordinate with the metal ions. It may presumably be due to the steric hinderance of the ligand.

Tritylthionitrite reacted with a number of metal ions and their complexes in presence of HCl gas or  $\text{HgCl}_2$  at elevated temperatures to yield metal nitrosyls. On reacting with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  and its complexes instead of forming  $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ , it yielded sulfido nitrosyl complexes. Though  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  and  $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$  yielded pure nitrosyl complexes, but the yields were very poor. It suggests that in the absence of HCl or  $\text{HgCl}_2$ , the decomposition of trityl thionitrite is not smooth and the concentration of NO, is relatively poor than needed for the formation of more stable nitrosyl complexes. Because of very high stability towards dissociation (equilibrium lying towards nitrosation) at room or lower temperature, the reactions of trityl thionitrite with some metal ions and their complexes and particularly those whose nitrosyls are formed only at low temperatures could not afford their nitrosyls. The same reactions were carried out at lower temperatures also but, with negative results. This is not unexpected because of the stability of the thionitrite at low temperatures.

Nitrosylation reactions involving S-nitrosocysteine as a nitrosylating agent, yielded pure nitrosyl complexes only in presence of  $\text{HgCl}_2$ . In its absence nitrosyls containing cystine as one of the ligands were obtained at elevated temperatures. The stability of S-nitrosocysteine is not high and it rapidly dissociates to nitric oxide and cystine, we could, therefore, be able to

synthesize a few of the cobalt nitrosyls at room temperature. suggesting the suitability of S-nitrosocysteine for the nitrosylation reactions at higher and in a few cases at room temperature also.

Reactions of S-nitrosothiourea with different metal ions and their complexes in presence of different ligands yielded mostly thiocyanato complexes rather than nitrosyls. Though it formed nitrosyls with those metal ions having very high affinity for NO but NCS group was invariably present in all the complexes. Depending upon the pH of the reaction medium, nitrosothiourea decomposes through, two pathways leading to the formation of both NO, and HNCS (cf. Chapter Five).



The results indicated that the reactions of metal ions with HNCS is more effective than the trapping of NO. The reason could be that the formation of  $\text{NCS}^-$  complexes is so fast that before NO is picked up by the metal ions for nitrosylation (cf. mechanism 2) it migrates to the N atom of thiourea with the subsequent formation

of  $\text{NCS}^-$  ion by destroying  $\text{NO}^+$  group. The process will further increase the concentration of  $\text{NCS}^-$  ion resulting in lowering  $\text{NO}$  concentration further. Thus the higher concentration of  $\text{NCS}^-$  coupled with its better coordinating ability may be responsible for the formation of thiocyanato complexes rather than metal nitrosyl. Thus nitrosothiourea does not appear to be a good nitrosylating agent.

From the above discussion it is obvious that penicillamine and trityl thionitrites can be utilized as nitrosylating agents in a more or less generalized way preferably at higher temperatures. Trityl thionitrite works better in presence of catalysts like  $\text{HCl}$  or  $\text{HgCl}_2$ . S-nitrosocysteine nitrosylates the metal ions both at elevated and room temperature, but is not very effective. Nitrosothiourea may not be preferentially utilized in nitrosylation reactions, because of the formation of thiocyanato complexes in most of the cases. Nitrosyl complexes are formed only in those cases where metal ions have a great affinity for  $\text{NO}$ .

## CHAPTER EIGHT

### SUMMARY AND SCOPE FOR FUTURE WORK

During the past couple of decades, the chemistry of transition metal nitrosyls has outgrown to its bursting point. A large activity by the chemists in this area have probably been due to (a) their peculiar nature of bonding with the metal (b) their unusual reactivity (c) their catalytic properties (d) their applications in pollution control and (e) their potential use as precursors in organic syntheses. In addition, transition metal nitrosyls provide as a very effective tool in order to understand the energetics of nitrogen fixation and the reactions of molecules which play a vital role in the living systems.

Although a number of synthetic procedures for the metal nitrosyls are available in the literature, the interaction of gaseous NO with the metal ions and their complexes is still preferentially adopted for their synthesis. On the contrary, the

thermodynamic instability of NO coupled with its being a menacing pollutant sometimes puts a constraint on its generalized application. One is therefore, bound to rethink towards the development of new procedures for the metal nitrosyl synthesis. One of the possible routes could be in situ generation of NO by cleaving weak S-NO or O-NO bond in thionitrite or alkyl nitrite respectively with subsequent trapping of the generated NO by the metal ions. The present thesis embodies the results of an attempt in this direction.

First chapter of the thesis describes briefly the objectives and the scope of the work. It highlights an overview of the transition metal nitrosyl chemistry describing (a) various synthetic methods so far adopted for the transition metal nitrosyls, (b) their activity (c) bonding modes of NO group with the metal ions and (d) different theories, rules and techniques propounded by the chemists in order to understand and distinguish between linear and bent M-NO groups.

Second chapter of the thesis describes a new generalised synthetic procedure for the synthesis of transition metal nitrosyls. Advantage have been taken of the weakness of S-NO bond of the N-acetyl-dl-penicillamine thionitrite which is readily cleaved in the medium. It generates NO in the medium of the reaction, which is subsequently trapped by the metal ions or their complexes. The reactions of penicillamine thionitrite have been carried out with different metal salts,  $MCl_3 \cdot xH_2O$  ( $M = Ru, Rh, Ir$ ), Co, and Mo

in presence of coligands like  $\text{PPh}_3$ ,  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ ,  $\text{P(OPh)}_3$ , and ethylenediamine and with the complexes of Ru and Rh. The latter reactions were also performed in presence of dry HCl gas or  $\text{HgCl}_2$ . Which possibly catalyse the denitrosation of thionitrites, besides providing the source of chloride ions. It was observed that the nitrosylation reaction proceeded smoothly both in presence or in the absence of  $\text{HgCl}_2$  and HCl gas. The nitrosylating properties of penicillamine thionitrite have been compared to those of the best known nitrosylating agent viz, MNTS at elevated temperatures. The results of the reactions carried out revealed that the penicillamine thionitrite, at higher temperature appears to be a very versatile nitrosylating agent compared to MNTS, if not better.

Third chapter envelopes the reactions of trityl thionitrite with different metal salts, viz.  $\text{MCl}_3 \cdot x\text{H}_2\text{O}$  ( $\text{M} = \text{Ru}, \text{Rh}, \text{Ir}$ ),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mo(CO)}_6$ ,  $\text{W(CO)}_6$ , chromous acetate, ammonium molybdate, potassium chromate, and ferrous sulfate in presence of coligands ( $\text{PPh}_3$ ,  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ , ethylenediamine, diethyldithiocarbamate, ammoniumthiocyanate, pyridine, bipyridyl and acetyl acetone) and with large number of ruthenium, rhodium and nickel complexes in presence of  $\text{HgCl}_2$ ,  $\text{Cl}_2$  or HCl gas. Tritylthionitrite thermally decomposes into NO radical and its disulfide at slightly higher temperatures ( $\approx 60^\circ\text{C}$ ). It was observed that the reactions of tritylthionitrite with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylphosphine and ruthenium complexes led to the syntheses of pure nitrosyl complexes only in the presence of dry HCl gas or  $\text{HgCl}_2$  at elevated

temperatures. In the absence of the latter compounds it yielded a complex containing sulfide. Reaction of tritylthionitrite with  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  and  $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$  in presence of triphenylphosphine and dry  $\text{HCl}$  gas or  $\text{HgCl}_2$  yielded pure nitrosyl complexes  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$  and  $[\text{Ir}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$  respectively. The same reactions in the absence of  $\text{HCl}$  gas yielded  $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$  and  $[\text{Ir}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ , but in very poor yields, suggesting that in the denitrosation of tritylthionitrite,  $\text{HgCl}_2$  or  $\text{HCl}$  plays very important role and their presence is necessary for the better yields of nitrosyls. Reactions of tritylthionitrite with  $\text{Cr}(\text{II})$ ,  $\text{Co}(\text{II})$ ,  $\text{Fe}(\text{II})$  and molybdenum in presence of different coligands at room and low temperatures could not yield the nitrosyls. Obviously the denitrosation reaction of tritylthionitrite does not seem to be very favourable at room or low temperatures. One may therefore conclude that the tritylthionitrite has a large potentiality for metal nitrosation only at relatively higher temperatures.

Chapter four deals with the products, resulted from the reactions of S-nitrosocysteine with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  in presence of  $\text{PPh}_3$ ,  $[\text{RuCl}_2(\text{PPh}_3)_3]$ ,  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  in presence of  $\text{PPh}_3$  and  $[\text{RhCl}(\text{PPh}_3)_3]$  in the presence and absence of  $\text{HgCl}_2$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in the presence of bipy and lithium perchlorate. It was observed that the reactions in the presence of  $\text{HgCl}_2$  yielded pure nitrosyl complexes while in the absence they gave nitrosyls containing cystine. Reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  afforded pure literature known nitrosyl complex  $[\text{Co}(\text{NO})(\text{Bipy})_2\text{Cl}]\text{ClO}_4$ .

Chapter five describes the reactions of S-nitrosothiourea with a number of transition metal ions and their complexes in presence of different colligands under varying reaction conditions. It was observed that the reaction of metal ions with nitrosothiourea yielded mostly thiocyanato complexes. Only a few reactions gave pure nitrosyls and particularly with the metal ions having great affinity for NO. There are following two parallel decomposing reactions of nitrosothiourea. In these reactions the one yielding HNCS dominates the reaction path, while the second one goes with the metal ions having high affinity for NO.

Reactions of methyl, ethyl, propyl and n-butyl nitrites with the metal ions of Cr, Fe, Co and a few of their complexes in presence of different colligands at room and low temperatures have been described in chapter six of the thesis. The results indicated the potential applicability of alkyl nitrites as nitrosylating agent for the transition metal nitrosyl synthesis at low temperatures also.

Chapter seventh describes briefly a comparison of reactivities of penicillamine thionitrite, tritylthionitrite, S-nitrosocysteine and S-nitrosothiourea towards nitrosylation reactions with the metal ions.

Following are some of the problems related to the present work which may be taken in future.

1. The nitrosylating properties of  $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \diagup \\ \text{CH}_3 \end{array} \text{C-S-NO}$  along with other thionitrites stable at room temperatures.

2. The metal nitrosylation by thionitrites having different substituents attached to the carbon  $\begin{matrix} R_1 \\ R_2 \\ R_3 \end{matrix} \rightarrow C-S-NO$  (where  $R_1=R_2=C_6H_5$  and  $R_3=CH_3$ ) will be taken up. The effect of the substituents on the metal nitrosylation will be examined. Thereby it will be possible to find a particular nitrosylating agent which may work at all the temperatures and under different reaction conditions.
3. The oxidative addition reactions between  $16 e^- d^8$  nitrosyl complexes and  $RONO$  ( $R$ =alkyl or aryl group) which may lead to the formation of interesting transition metal alkoxides.
4. The nitrosylation properties of the compounds containing  $C-NO$  will be examined.
5. The compounds containing  $M-NO$  ( $M$ =any non metal) will also be examined. The work on nitrosylation using  $P-NO$  is still in an embryonic state and it should be further explored.

List of Publications

1. In Situ Trapping of NO: Application of S. Nitrosoderivative for metal Nitrosyl Synthesis.  
D.S. Pandey, S.K. Saini and U.C. Agarwala  
Bull. Chem. Soc. Jpn., 60, 3031-3033 (1987).
2. Alkyl Nitrites as Nitrosylating agents.  
D.S. Pandey, M.I. Khan and U.C. Agarwala  
Indian Journal of Chemistry 26A, 570-573 (1987).
3. Transition Metal Complexes As Antimicrobial agents.  
D.S. Pandey, Lallan Mishra and U.C. Agarwala  
(communicated).
4. A generalised Method for the synthesis of transition metal nitrosyl Using Organic N-Nitroso derivatives as Nitrosylating agents.  
D.S. Pandey, M.I. Khan and U.C. Agarwala  
Inorganica Chimica Acta. (communicated).
5. Penicillamine thionitrite - A potential nitrosylating agent  
D.S. Pandey and U.C. Agarwala  
J. Chem. Soc. Dalton Trans. (communicated).
6. In Situ Trapping of NO: Application of Trityl Thionitrite for metal nitrosyl synthesis.  
D.S. Pandey and U.C. Agarwala  
Canadian Journal of Chemistry (communicated).
7. Nitrosothiourea: Its Reactivity with Metal Ions and their complexes.  
D.S. Pandey and U.C. Agarwala  
Polyhedron (communicated).